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The U.S. Environmental Protection Agency Asbestos-in-Schools Program was established in March, 1979 to provide information and technical assistance to the public for addressing problems presented by asbestos-containing insulation materials in school buildings. Because there were no existing standard procedures for the qualitative and quantitative analysis of asbestos in bulk materials, the Office of Pesticides and Toxic Substances, Washington, DC, and the Environmental Monitoring Systems Laboratory, Research Triangle Park, NC, jointly sponsored an effort to produce a practical and objective analytical protocol. Draft procedures were written for the analysis of bulk samples by polarized light microscopy (PLM) and X-Ray powder diffraction (XRD). Following review, the Tentative Method for the Determination of Asbestiform Minerals in Bulk Insulation Samples (March, 1980) was submitted to a performance testing program that involved multiple laboratory analysis of prepared samples with known asbestos content. This report presents the results of the testing study and provides observations and preliminary characterization of the utility and operational parameters of the Tentative Method.

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FOREWORD

Measurement and monitoring research efforts are designed to anticipate potential environmental problems, to support regulatory actions by developing an in-depth understanding of the nature and processes that impact health and the ecology, to provide innovative means of monitoring compliance with regulations, and to evaluate the effectiveness of health and environmental protection efforts through the monitoring of long-term trends. The Environmental Monitoring Systems Laboratory, Research Triangle Park, North Carolina, is responsible for: assessing environmental monitoring technology and systems; implementing Agency-wide quality assurance programs for air pollution measurement systems; and supplying technical support to other groups in the Agency including the Office of Air, Noise, and Radiation, the Office of Pesticides and Toxic Substances, and the Office of Enforcement.

This report describes the results of an evaluation of a tentative method developed for the measurement of asbestos in bulk insulation materials. The method is designed to support the Asbestos-in-Schools Program of the Office of Pesticides and Toxic Substances.

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ABSTRACT

The U.S. Environmental Protection Agency Asbestos-in-Schools Program was established in March 1979 to provide information and technical assistance to the public for addressing problems presented by asbestos-containing insulation materials in school buildings. Because there were no existing standard procedures for the qualitative and quantitative analysis of asbestos in bulk materials, the Office of Pesticides and Toxic Substances, Washington, DC, and the Environmental Monitoring Systems Laboratory, Research Triangle Park, NC, jointly sponsored an effort to produce a practical and objective analytical protocol.

Draft procedures were written for the analysis of bulk samples by polarized light microscopy (PLM) and X-ray powder diffraction (XRD) based on information presented at a conference of interested parties from government, university, and commercial laboratories. Following review by the conferees, the Tentative Method for the Determination of Asbestiform Minerals in Bulk Insulation Samples (March 1980) was submitted to a performance testing program that involved multiple laboratory analysis of prepared samples with known asbestos content. This report presents the results of the testing study and provides observations and preliminary characterization of the utility and operational parameters of the Tentative Method.

PLM quantitative analysis employs a point counting procedure to estimate the relative area occupied by asbestos fiber within the microscope fields of view. This must be compared with the known weight of asbestos in the sample in order to characterize the accuracy of the method. Data produced by the point counting procedure are compared with those produced by the typical quantitation procedures used by some of the participating laboratories. Accuracy and precision of the point counting procedure are considered in two contexts: (1) as PLM is currently used, regarding reported data as a direct estimate of weight percent of asbestos present; and (2) allowing adjustments of the data to account for bias and variance in the relationship between the relative area occupied by asbestos and the known weight percent of asbestos in the sample. Information is also presented on within-laboratory variance and the frequency of false negatives and false positives.

A very limited amount of data was returned for characterizing the XRD protocol. Both thin-layer and thick-layer (bulk) techniques were used for quantitative XRD analysis. Because of the small number of XRD reports, and the nonequivalence of methods employed, it is not possible to draw any firm conclusions on the precision and accuracy of the XRD protocol. A general comparison of bulk and thin-layer techniques with respect to precision, accuracy, and sensitivity is made.

Comments received from participating laboratories and recommendations for continued investigation of asbestos bulk sample analysis are presented.

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SECTION 1

INTRODUCTION

Inhalation of asbestos fibers was first recognized and managed as an occupational health hazard in Great Britain. Epidemiological and experimental studies have since provided extensive evidence of increased risk of pulmonary fibrotic disease (asbestosis), pleural and peritoneal mesothelioma, and other carcinomas due to both occupational and nonoccupational exposure to asbestos fiber.[1]

The U.S. Environmental Protection Agency (EPA), in cooperation with the Consumer Product Safety Commission and other Federal agencies, has investigated the potential for hazardous exposures from asbestos-containing products. The life-cycle of manufactured goods was followed from mining and milling of asbestos ore through disposal of the used manufactured products. Significant exposures were discovered in several use categories, including the application of sprayed-on insulations, application of patching plaster, and use of asbestos filters in food and drug processing.

The U.S. Government has sought to limit exposure to asbestos through a variety of legislative and regulatory actions.[2] Asbestos was listed as a potential hazardous air pollutant in 1971 (36 FR 5931) and airborne emissions were regulated under the Clean Air Act in 1973 (38 FR 8820). Most notable to this study was the action taken in April 1973 to ban the spray application of insulation products containing more than 1 percent asbestos by weight (38 FR 8820).

In March 1979, EPA established the Asbestos-in-Schools Program to provide information and technical assistance to the public for addressing the problems presented by asbestos-containing materials in school buildings (44 FR 54676). EPA has published several guidance documents[3] [4] that contain technical information on the identification and control of potential exposures to asbestos fibers. The guidance documents and other information are available through toll-free telephone numbers maintained by the Research Triangle Institute and the EPA Office of Pesticides and Toxic Substances (OPTS) Industry Assistance Office. Additional assistance is available from EPA-designated Regional Asbestos Coordinators.

EPA has recommended that polarized light microscopy (PLM) be used for estimating the asbestos content of bulk samples, to be supplemented with X-ray powder diffraction (XRD) should additional information on the sample be required.[3] Part I of the guidance document includes guidelines for PLM and XRD analysis, but notes the lack of standard protocols for either PLM or XRD. It also notes the absence of any program for qualification of PLM or XRD laboratories. (Since publication of the document, EPA has established a voluntary quality assurance program[5] for laboratories capable of PLM analysis of bulk samples. Information on the program may be obtained from RTI.)

Because there were no existing standard procedures for the qualitative or quantitative analysis of asbestos in bulk materials, the Office of Pesticides and Toxic Substances, Washington, DC, and the Environmental Monitoring Systems Laboratory, Research Triangle Park, NC, jointly sponsored an effort to produce a practical and objective analytical protocol. The task was initiated by reviewing existing literature and conferring with recognized experts in the field. Results of this survey indicated that PLM is the most appropriate analytical method, to be augmented by XRD when necessary.

In an effort to optimize the application of these techniques to the specialized task at hand, a conference of knowledgeable and interested parties from government, university, and commercial laboratories was convened. The symposium "Methods Definition for the Polarized Light Microscope and X-Ray Diffraction Analysis of Bulk Samples for Asbestos" was held at the U.S. Bureau of Mines, Avondale Research Center, Avondale, MD, on October 23-24, 1979 (see Appendix E for attendees). Conferees discussed techniques for sample preparation and qualitative and quantitative analysis by both PLM and XRD.

Following this conference, PLM and XRD analytical procedures were drafted to reflect the best inputs or consensus agreements of the conferees. Drafts were subsequently circulated twice for review by conference participants and other professionals active in the analysis of asbestos. Following review, the Tentative Method for the Determination of Asbestiform Minerals in Bulk Insulation Samples (March 1980) was submitted to a performance testing program that involved multiple laboratory analysis of real-world samples and prepared samples with known asbestos content. This report presents the results of the testing program and provides preliminary observations and characterization of the Tentative Method's utility and operational parameters. Recommendations for revision of the Tentative Method and for further investigation of PLM and XRD analysis are also presented.

Revisions pursuant to the recommendations of this report and the comments received in the evaluation study have been incorporated into the method. The current revision of the method may be found in the EPA report Interim Method for the Determination of Asbestos in Bulk Insulation Samples (October 1981).

SECTION 2

SUMMARY

An interlaboratory study was conducted to evaluate the accuracy, precision, and general utility of the Tentative Method for the Determination of Asbestiform Minerals in Bulk Insulation Samples (March 1980). Twenty-two commercial and four government laboratories were each supplied with eleven samples. Eight of the samples were formulated with a known weight of amosite or chrysotile and a matrix material containing primarily gypsum. Within-laboratory duplicates, blanks, and "real-world" samples of sprayed insulation were also included in the materials distributed to laboratories. Four laboratories (two commercial, two government) chose not to participate in the study. The twenty-two participating laboratories provided a total of thirty PLM reports and six XRD reports.

The Tentative Method includes procedures for qualitative and quantitative analysis of bulk samples by polarized light microscopy (PLM) and X-ray powder diffraction (XRD). Identification of asbestos fibers by PLM requires the observation of six optical properties: morphology, color and pleochroism, refractive indices (or dispersion staining colors), birefringence, extinction characteristics, and sign of elongation. PLM quantitative analysis uses a point counting procedure to estimate the percent area occupied by asbestos fibers within the microscope fields of view. The prepared samples distributed in this study contained a known weight percent of asbestos. Because PLM analysis produces an estimate of the relative area occupied by asbestos, the relationship between reported area percent and the known weight percent of asbestos was investigated.

Reported area percent data are best correlated with the known weight percent values when regressions are performed in natural logarithmic coordinates, indicating that the relationship between area and weight involves a power transformation. Analysis of the regression shows that variation in the relationship is attributable to differences between laboratories and to differences between asbestos types (chrysotile and amosite).

Reported PLM data were divided into three groups based on the quantitation procedure(s) used by the reporting laboratory.

Group P--(Point count) PLM asbestos area percent determinations by the point count procedure (Interim Method).

Group B--(Both) PLM asbestos area percent determinations by the laboratories' own methods for laboratories that also provided data by the point count method.

Group O--(Other) PLM asbestos area percent determinations by the laboratories' own methods for laboratories declining to use the point count method.

Data in Group O (other) contributed by different laboratories were not necessarily produced by the same quantitation procedure. Six laboratories that contributed data to Group P (point count) also reported results produced by their own quantitation procedures. This data set is designated Group B (both). Four of the laboratories produced closer estimates of the true weight percents by their own method than by point counting, while the other two laboratories reported closer results by point counting. It is unclear what, if any, relationship exists between the Group P and Group B data contributed by any one laboratory. It is possible that an estimate produced by point counting could have influenced a laboratory's own procedure, or vice versa.

Considering reported PLM results as direct estimates of the weight percent of asbestos present, it was found that Group O (other) is significantly more biased than Group P (point count). Groups P and B (both) are similarly biased. Point counting has a greater positive bias on amosite samples than on chrysotile samples. For a sample containing 10 percent chrysotile by weight, the average bias (b) of Group P (point count) is 18.5 percent; for 50 percent chrysotile, b = -24.2 percent; for 10 percent amosite, b = 118.5 percent; for 50 percent amosite, b = 12.1 percent.

A regression relating standard deviations and means of reported results, when performed in natural logarithmic coordinates, did not establish any difference between Groups P, B, and O with respect to precision. The standard deviation of Group P (point count) is directly related to the mean reported value, and thus precision may be expressed as the coefficient of variation (CV). The CV is less than 100 percent on samples containing more than approximately 6 percent asbestos by area, and less than 50 percent on samples containing more than approximately 32 percent asbestos by area. At a mean reported value (MP) of 10 percent asbestos, CV ≅ 79 percent; at MP = 20 percent, CV ≅ 61 percent; at MP = 50 percent, CV ≅ 41 percent.

To investigate improvements in data quality that might be made by adjusting (calibrating) individual laboratory results, analyses were performed on transformed data. If the parameters of the area-weight relationship are used to transform reported area percent data to predicted weights, a considerable gain in accuracy is achieved, as measured by the average percent absolute error. By this measure of accuracy, Group O (other) has a greater error than Group P (point count) on samples containing less than 20 percent asbestos by weight. Residual variance in the transformed data is measured by the mean squared error about the regression. Group P was found to be significantly more precise than Groups B and O. Further analysis of adjusted data indicates that laboratories using point count analysis are better able to distinguish samples containing more than 7 percent from those with less than 7 percent asbestos by weight than they are able to distinguish samples with more than 1 percent from those with less than 1 percent asbestos by weight.

Samples from the chrysotile series were included as within-laboratory duplicates. Although a more extensive effort would be required to adequately evaluate the precision of the PLM protocol on repeated analysis of the same sample, a gross estimate using the present data indicates that within-analyst variability accounts for less than 25 percent of the total variance.

Data produced by point counting included five false negatives out of a total of 19 analyses of the 1.2 percent chrysotile sample. One false negative out of 19 analyses was reported for the 4.9 percent chrysotile sample. No false negatives were reported for any amosite samples or for any samples containing more than 5 percent chrysotile by weight. The reporting of false negatives is more likely due to the variability of sample and slide preparation steps than to the point counting procedure per se. One false positive out of 19 analyses was reported for the series of blank samples and was probably due to contamination. The probability of a false negative on the 4.9 percent chrysotile sample was 0.05 (1/19). EPA currently recommends the analysis of at least three samples of a suspect material. The rate of false negatives is such that the analysis of three samples, if each contained at least 5 percent asbestos by weight, would result in three false negatives with a probability less than 0.03 and possibly as low as 0.001.

Identification of sample components by XRD analysis is accomplished by comparison of the sample diffraction pattern with standard reference powder diffraction patterns. Quantitative analysis involves measuring the integrated areas of diagnostic peaks selected from the full XRD scan of a thin-layer sample. Quantitative analysis must include a correction for matrix absorption effects and comparison with suitable external standards. XRD affords information only on crystal lattice structure and not on crystal morphology. XRD analysis, therefore, cannot distinguish between asbestos minerals and their non-asbestiform varieties. The presence of fibrous particles in a sample must be determined by an optical technique such as PLM.

The six laboratories reporting XRD results were grouped into two general categories for purposes of data analysis. These categories, thin-layer and bulk, were defined on the basis of the XRD technique used for quantitative analysis. Three of the laboratories performed the requested analyses using some variation of the thin-layer method of quantitation included in the Tentative Method. The remaining three laboratories used alternative bulk or thick-layer methods of quantitation. It should be emphasized that within categories none of the methods used were strictly equivalent. Moreover, within the thin-layer group, no laboratory followed the Tentative Method protocol exactly.

Because of the small number of participating laboratories reporting XRD results, and the nonequivalence of methods employed, it is not possible to draw any firm conclusions from the reported results about the accuracy and precision of the XRD method. However, from a general comparison of bulk vs. thin-layer methodology, the following observations can be made:

1. The bulk method appears to be at least as accurate and precise as the thin-layer method over the range of samples included in this study and significantly more accurate for the analysis of chrysotile; and
2. There is a suggestion that the thin-layer method of analysis may be more reliable (i.e., more sensitive) than the bulk method at the 1 percent level of chrysotile in a simple matrix.

Data produced by thin-layer methods of analysis included one false negative out of three analyses of the 4.9 percent chrysotile sample. The same laboratory reported chrysotile false positives for all amosite samples and for the blank sample with reported chrysotile values ranging from <1 to 8 percent. A second laboratory reported one false negative out of three analyses in the 19.4 percent chrysotile sample.

Data produced by bulk methods of analysis included two false negatives out of three analyses of the 1.2 percent chrysotile sample. One of these laboratories also reported a false positive amosite in the 4.9 percent chrysotile sample.

SECTION 3

RECOMMENDATIONS

The study presented in this report is a preliminary evaluation designed to determine the precision and accuracy of the Tentative Method as applied to carefully prepared samples. It should be emphasized that the samples analyzed consisted of only two types of asbestos fiber and a single matrix material. Only one type of asbestos was included in any given sample. One of the main obstacles to reliable analysis of bulk samples is the variability of sample composition. Complete characterization of the method presented herein requires that several issues be addressed, as discussed below. The highest priority, however, should be assigned to investigations that will extend the application of the method to a range of real-world samples involving different fiber types and matrices.

3.1 POLARIZED LIGHT MICROSCOPY

Several aspects of the PLM method require further investigation. Briefly, future studies should be designed to determine the following:

1. The feasibility of specifying definitive sample preparation procedures to be used prior to quantitative PLM analysis;
2. The proportion of total variance attributable to individual procedures of the method, i.e., sample preparation, subsampling, and point counting;
3. The proportion of total variance contributed by within-laboratory variability;
4. The effect of specific variables within the point counting procedure, including the number of points to be counted, magnification used, and the possible bias introduced by the use of a 25-point reticle instead of a cross-hair reticle;
5. The possibility of introducing a staged point counting process that would allow fewer counts to be determined on samples with a high percentage of asbestos;

6. The effect of more than one type of asbestos being present in a bulk sample;

7. The feasibility of individually calibrating PLM laboratories with information derived in round robin sample analysis programs.

The protocol supplied to laboratories in this study contained a provision for reporting less than 1 percent asbestos in a sample if fewer than 7 of 400 points are scored for asbestos (Appendix B, PLM p. 8). This provision was based on an approach to the data involving hypothesis testing and on the assumption that results of repeated analysis of samples with small amounts of asbestos would fit a Poisson distribution. Sufficient data are not currently available to support the Poisson assumption for analysis of "real-world" samples. Additionally, the hypothesis testing approach is not appropriate to the typical use of laboratory data. It is therefore recommended that the provision be deleted and that the simple arithmetic percentage be used for determining asbestos content at all levels.

The confidence interval calculation (Appendix B, PLM p. 9) presently included in the PLM protocol is misleading. It does provide a good estimate of reliable bounds for the relative area occupied by asbestos fiber in the examined fields of view. However, because of other sources of variation (sampling, subsampling, sample and slide preparation), the confidence interval may not be thought of as reliable bounds for the percent asbestos in the material from which the sample was taken. It is therefore suggested that the calculation of the confidence interval be deleted from the method.

Finally, it is apparent from the results of this study that some type of training would be required to achieve comparable application of the PLM protocol between laboratories. While point counting is a classical petrographic technique, it is not a standard procedure in the majority of laboratories currently analyzing bulk samples for asbestos. Training alternatives might include regional courses and distribution of split samples analogous to the NIOSH program for the asbestos air sampling method.

It should also be noted that the PLM method presented, although an improvement over subjective techniques, is still a procedure for estimating the relative area occupied by asbestos fiber and matrix material, and requires an area-to-weight conversion to apply to the Federal standard (38 FR 8820). Alternative analytical techniques that measure weight percent directly or that provide an empirically more satisfying relationship to relative weight of asbestos fiber should be sought and investigated.

3.2—X-RAY POWDER DIFFRACTION

There are two major areas in the application of XRD techniques to quantitative analysis of asbestiform minerals in bulk materials that require further investigation: (1) identification and characterization of standard reference materials, and (2) further development and evaluation of thin-layer and bulk methods of analysis.

3.2.1 Identification and Characterization of Standard Reference Materials

The most common concern of laboratories participating in the evaluation of the XRD protocol was the lack of well-characterized, readily available reference materials. Both NIOSH[6] and the Bureau of Mines[7] have conducted rather extensive studies in this area; however, these materials are not available in large quantities for general use. In addition, the UICC standards* are not exceptionally pure and have been reported to be in dwindling supply. Therefore, a thorough, systematic investigation of asbestiform minerals for use as standard materials should be undertaken. This should include identification of major sources; determination of availability and cost; and complete mineralogical characterization and determination of purity, particle size distributions, and powder diffraction patterns of materials from these sources.

Since asbestos minerals vary in composition depending on the source and exhibit different behaviors in grinding, peak positions and/or relative intensities of XRD patterns may vary from sample to sample. This variability is particularly problematic for the amphibole minerals. A quantitative study to assess the comparability of X-ray response of asbestos minerals from different sources should be conducted. If possible, observed differences between different samples of the same asbestos variety should be correlated with specific sample characteristics (e.g., chemical composition and particle size).

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*Prepared by the International Union Against Cancer. Available from: UICC, MRC Pneumoconiosis Unit, Llandough Hospital, Penarth, Glamorgan CF6IXW, UK, and commercial distributors.

3.2.2 Further Development and Evaluation of Thin-Layer and Bulk Methods of Analysis

The need for further development and evaluation of both thin-layer and bulk methods of XRD analysis is underscored by the following observations: few laboratories are currently set up to routinely perform the thin-layer analysis as prescribed; the proposed thin-layer method of quantitation is considerably more time-consuming and costly than bulk or thick-layer methods; and for samples analyzed in the methods evaluation study, the bulk method was at least as accurate and precise as the thin-layer method.

In particular, a comparison of the bulk and thin-layer methods should be made over a variety of asbestos types and matrix materials, with attention given to sample preparation requirements, instrument requirements, sensitivity, precision, accuracy, and speed and cost of analysis.

For both bulk and thin-layer methods, the following areas of investigation are proposed:

1. Assessment of sample preparation requirements--The requirement to grind the sample and standards to a comparable particle size of 10 μm is essential for rigorous quantitative analysis. It is recognized, however, that this is often time-consuming and costly and may not be feasible for some samples. In addition, since the matrix material itself may alter the grinding characteristics of the asbestos, the validity of standards prepared in a manner identical to the sample materials is questionable. A systematic investigation of the effects of various grinding and matrix reduction techniques (e.g., milling, ultrasonication) on the different asbestos minerals in a variety of "common" matrices should be conducted, and changes in relative peak intensities, peak profiles, and positions monitored as a function of such parameters as grinding time, temperature, and type of mill.

2. Assessment of preferred orientation effects on quantitative analysis--This should include evaluation of the dependence of preferred orientation effects on sample preparation techniques, sample particle size, and sample substrate. For bulk methods, filtration, back-packing, and pelletizing methods of sample preparation should be evaluated; for thin-layer methods, the effects of the filter medium and sample particle size should be investigated. This could be extended to include an assessment of the feasibility of preferentially orienting the sample fibers prior to analysis to maximize reproducibility, with evaluation of instrument requirements and applicability to routine screening programs.

3. Assessment of the effect of the use of the step-scanning mode of analysis on the limits of detection--This should be evaluated for both methods by comparing sensitivities obtained with and without step-scanning for each asbestos mineral in a variety of matrices.

4. Assessment of absorption correction requirements and techniques--The use of an internal standard for absorption correction should be systematically evaluated. For thin-layer methods of analysis, the internal correction should be compared with the proposed method of absorption correction by measurement of the attenuation of a silver filter substrate peak. Evaluation of the latter method of absorption correction requires further assessment by XRD of the variability of the silver content in silver membrane filters both between filters and between front and back sides of the same filter.

Since XRD offers the possibility of rapid, sensitive, automated analysis of asbestos at a time when a major increase in screening and monitoring efforts is projected, it is hoped that the results of such investigations will allow refinement of the present XRD method to one that is less costly, less time-consuming, and better suited to routine analysis of bulk materials.

SECTION 4

ANALYTICAL METHODS

A Tentative Method has been developed for the analysis of asbestos in bulk insulation materials by polarized light microscopy (PLM) and X-ray powder diffraction (XRD) techniques. The Tentative Method is presented in Appendix B. Procedures for qualitative and quantitative analysis have been included to address Federal regulations that limit the asbestos fiber content of sprayed insulation materials to 1 percent by weight (38 FR 8820).

Classical petrographic techniques are specified in the PLM protocol for identification of asbestos fibers and other components of bulk samples. Subsamples of bulk material are prepared by appropriate techniques, immersed in an oil of known refractive index, and examined with both single and crossed polars. Asbestos fibers are positively identified by the observation of six optical properties: morphology, color and pleochroism, refractive indices (or dispersion staining colors), birefringence, extinction characteristics, and sign of elongation.

There are several deterrents to the reliable quantitation of asbestos in bulk samples by PLM, including variable matrices, the small amount of sample examined, and variation in the optical properties of the asbestos minerals. Optical methods measure the relative area occupied by asbestos fiber and matrix material within the microscope fields of view. At present, most analysts using optical methods attempt the quantitation of asbestos either by visual estimation or by comparison of the microscope field of view with graphics prepared to correspond to area concentrations of 1 percent, 5 percent, 10 percent, etc. Such procedures have been shown in previous studies[8] to be highly variable because of differences among analysts in training, experience, and application.

Quantitation is performed in the PLM procedure by a point counting technique. Point sampling is used in various fields of study to estimate the relative area within specified boundaries occupied by a particular subject (type of rock, soil, plant, etc.). Point counting is used in petrography to estimate the relative areas of minerals in thin sections of rock. The technique assumes that particles within the field of view are of equal thickness and are randomly oriented with respect to the microscope light path.[9] Preliminary testing indicated that despite the violation of these assumptions by insulation materials, point counting might be applied to the quantitation of asbestos in bulk samples with less variability than previously used subjective techniques.

Qualitative analysis of bulk materials by XRD is performed with a minimum of matrix reduction. Samples are initially scanned over limited diagnostic peak regions for the serpentine (7.36 Å) and amphibole (8.2-8.5 Å) minerals, using standard slow-scanning methods for bulk sample analysis. All samples that exhibit diffraction peaks in the diagnostic peak regions for asbestiform minerals are submitted to a full (5°-60° 2θ; 1° 2θ/min) qualitative XRD scan. Typical X-ray powder diffraction patterns for individual sample components and for mixed samples are presented in Figure 1. Sample constituents are identified by comparison of the sample diffraction pattern with standard reference powder diffraction patterns. When subsequent quantitation is required, particular note is made of possible interferences.

The proposed thin-layer procedure for quantitation of asbestos in bulk samples by XRD is a modification of the NIOSH-recommended method for the analysis of chrysotile in air samples.[10] The procedure involves initial comminution of the bulk material to approximately 10 μm by cryogenic milling techniques and deposition of an accurately known amount of the sample on a silver membrane filter. The mass of asbestos is determined by measuring the integrated area of the selected diagnostic peak, correcting for matrix absorption effects, and comparing with suitable external standards. Analytical problems and limitations of the method are clearly identified in the protocol. Although there is ample evidence that this method is capable of measuring microgram quantities of asbestos in relatively simple systems with reasonable accuracy, precision, and speed,[11] its reliability for quantitative analysis of asbestos in bulk samples has not been fully characterized.

It should be emphasized that XRD affords information only on crystal lattice structure and not on gross crystal morphology. The XRD technique, therefore, cannot distinguish between the asbestos minerals and their nonasbestiform varieties. This can be demonstrated by comparing the diffraction patterns for antigorite (nonfibrous serpentine) and a mixed antigorite/chrysotile sample in Figure 1. Particle morphologies must be determined by an optical technique such as PLM. It is therefore recommended that XRD be used only as a corroborative procedure and not as an independent analytical method.

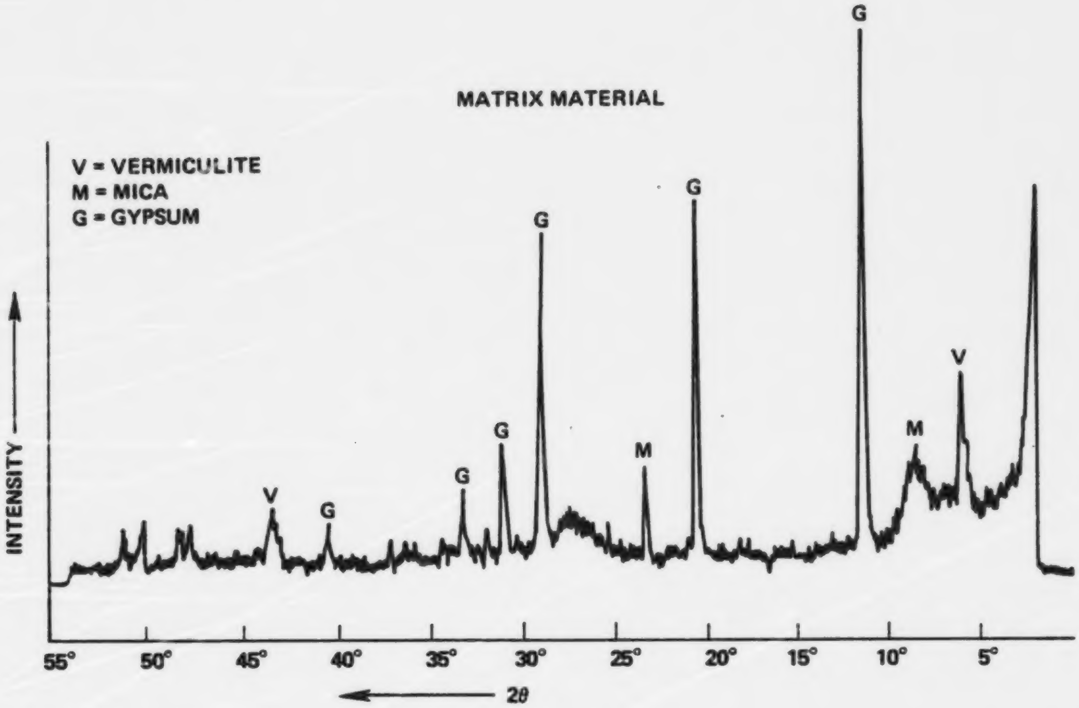
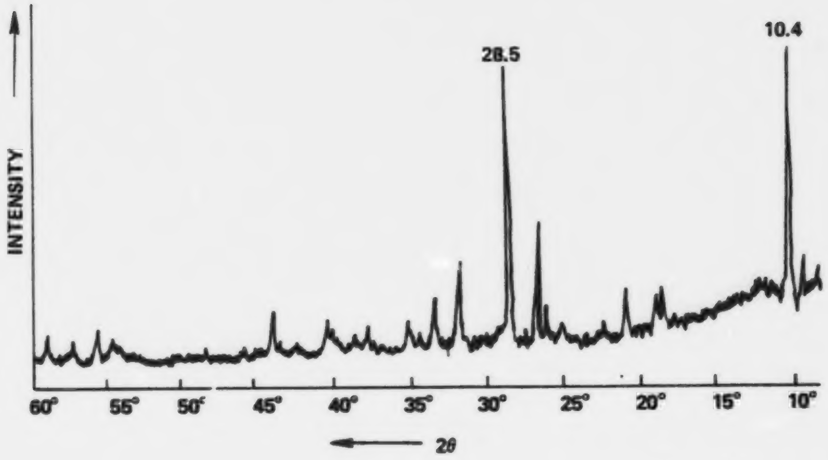


Figure 1. Examples of X-ray diffraction patterns.

AMOSITE



CHRYSOTILE

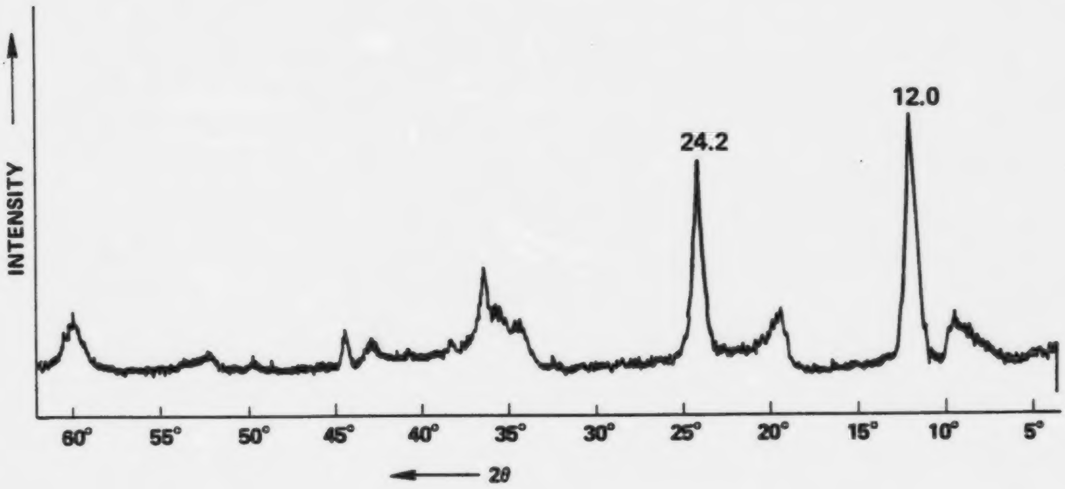
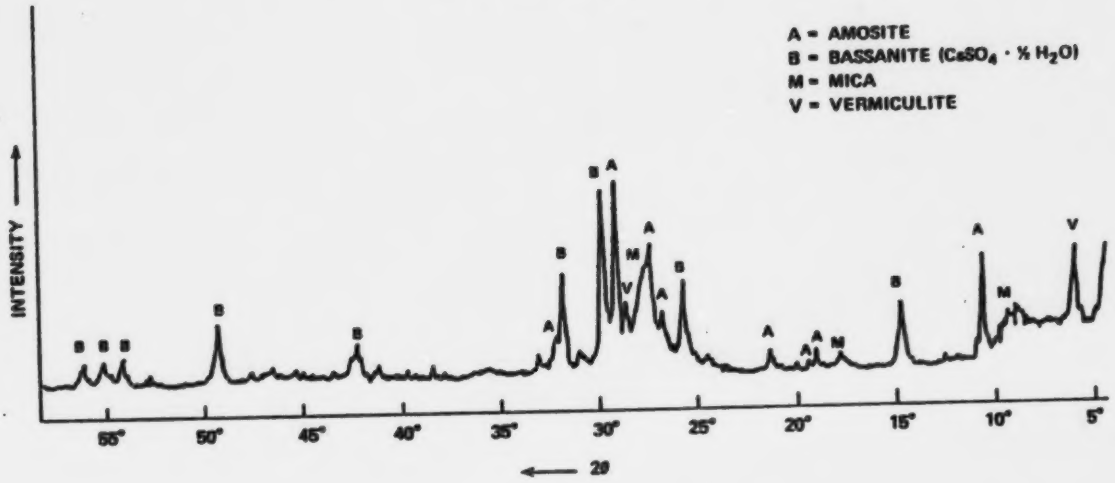


Figure 1 (continued)

SAMPLE SERIES D (19.4% AMOSITE)



SAMPLE SERIES E (19.4% CHRYSOTILE)

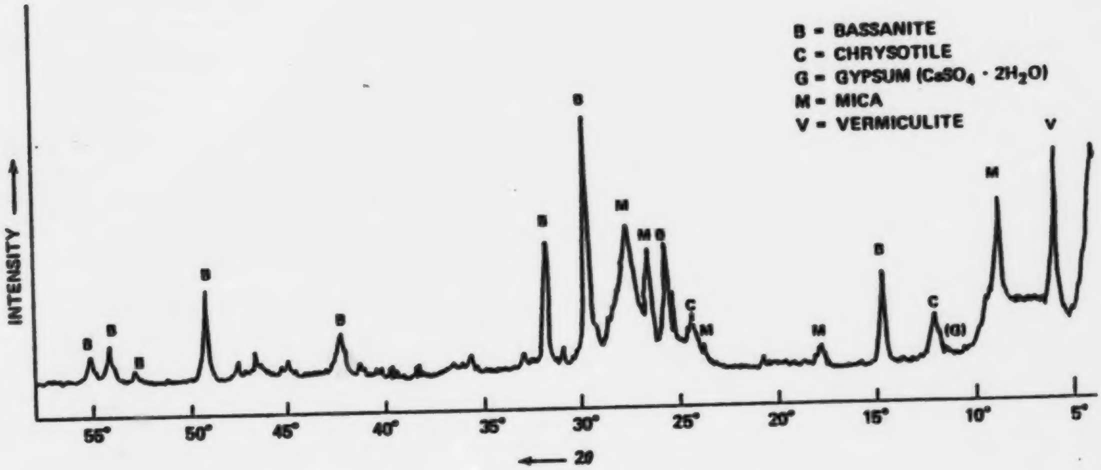


Figure 1 (continued)

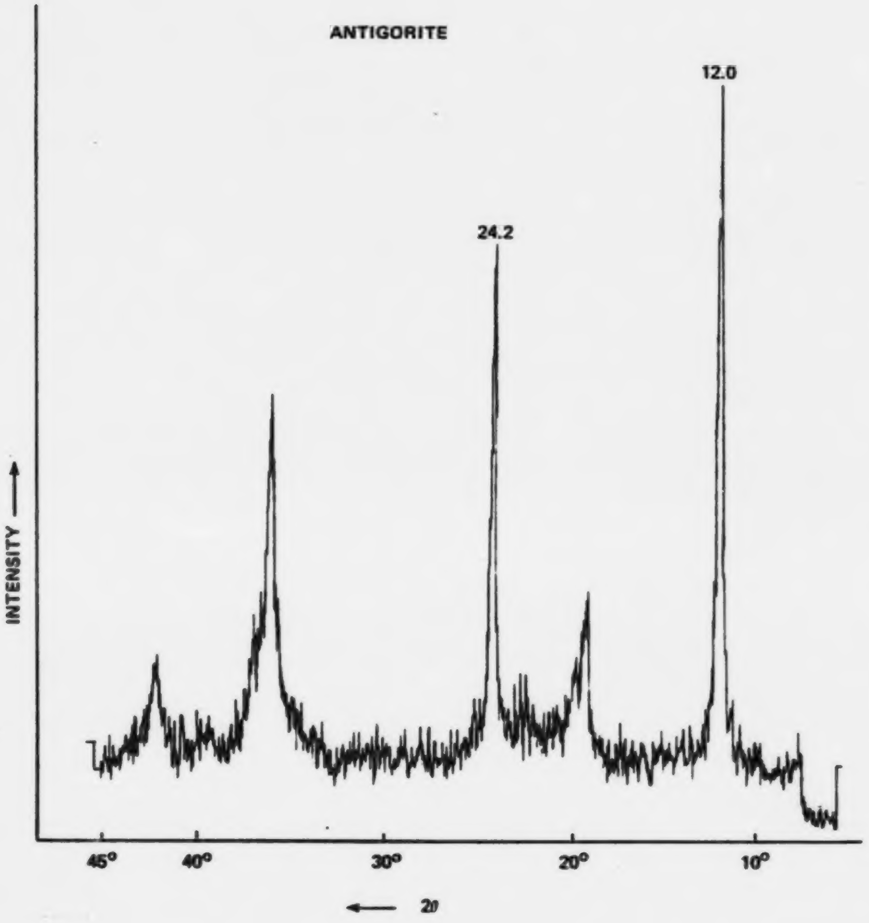


Figure 1 (continued)

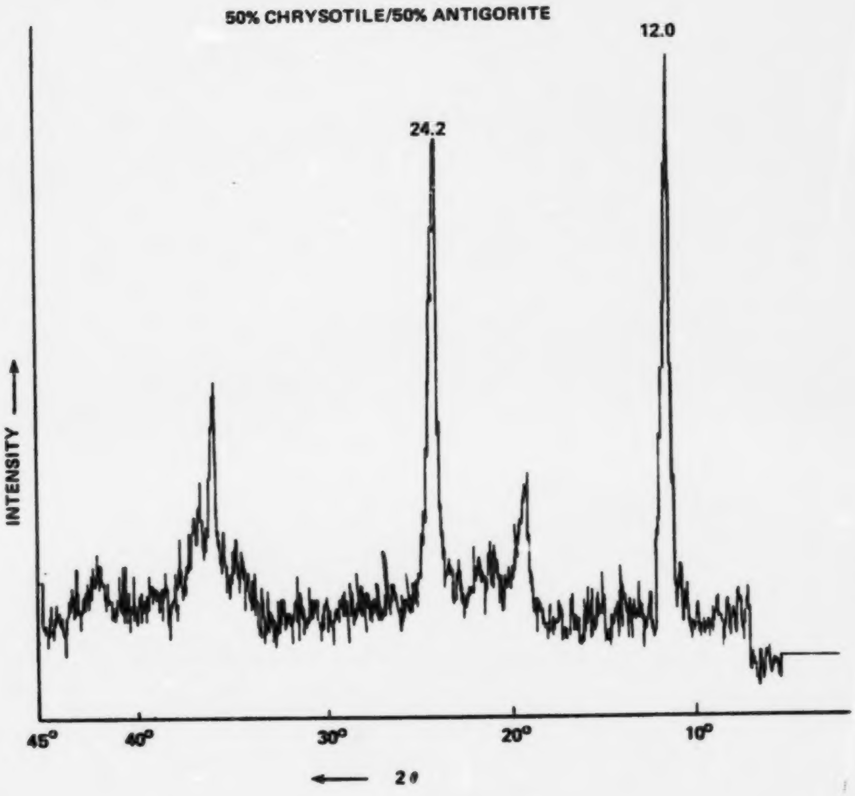


Figure 1 (continued)

SECTION 5

DESIGN OF THE EVALUATION STUDY AND DATA ANALYSIS

5.1 STUDY DESIGN

An interlaboratory testing program was designed and executed with the following objectives:

1. Evaluate the between-laboratory precision and accuracy and within-laboratory variation in applying the Tentative Method; and
2. Evaluate the error rate of the method relative to the Federal 1 percent weight criterion for asbestos content of sprayed-on insulation materials (38 FR 8820; April 6, 1973).

Twenty-two commercial and four government laboratories were each supplied with eleven samples. Eight of the samples were targeted at specific weight percents of asbestos fiber. Two species of asbestos were used, chrysotile and amosite. One matrix material, containing primarily gypsum, was used in all prepared samples. Target weights were designed to cover a wide range of asbestos concentrations approximately equally spaced on a logarithmic scale. Blanks (Series F) were provided as controls and for determining the method's potential for producing false positives. The "real-world" sample (Series J) was included for comparison of between-laboratory variance. Duplicates (Series K) were included to estimate the average within-laboratory variance. Target weights and allowable limits for matrix and asbestos fiber in each sample series are presented in Table 1.

Samples were assigned to laboratories by use of a permuted random number series. A list of participating laboratories is included as Appendix C. Cover letters, instruction sheets, and reporting forms are included as Appendix D.

5.2 SAMPLE PREPARATION

The following procedure was used for preparing each sample. Asbestos fiber was weighed onto either glassine paper or an aluminum boat, depending

TABLE 1. SAMPLE COMPOSITION

Series	Target wt. %	Actual wt. %	Fiber type	Wt. of asbestos (g)	Wt. of matrix (g)
C	1	1.2	Chrysotile	0.05 ± .005	4.95 ± .05
A	4	4.9	Chrysotile	0.20 ± .01	4.80 ± .05
E	16	19.4	Chrysotile	0.80 ± .01	4.20 ± .05
I	64	74.5	Chrysotile	3.20 ± .01	1.80 ± .05
H	2	2.5	Amosite	0.10 ± .01	4.90 ± .05
G	8	9.8	Amosite	0.40 ± .01	4.60 ± .05
D	16	19.4	Amosite	0.80 ± .01	4.20 ± .05
B	32	38.8	Amosite	1.60 ± .01	3.40 ± .05
F	0	0	None	None	3.0 - 5.0
J	-	50.0*	Chrysotile	-	-
K†	Varies	Varies	Chrysotile	-	-

*Mean of reported area percents, Groups P and B.

†Series K samples were provided as duplicates and included samples from series C, A, E, and I.

on the amount, and sealed until used. Matrix material was weighed into an aluminum boat and then sealed in a plastic sample bag until used. The asbestos was transferred from the glassine paper or aluminum boat to a beaker with deionized water, amended with 0.5 mL 1% sodium dodecyl sulfate (SDS) solution per 100 mL deionized water. The detergent solution was used to facilitate fiber dispersal and to reduce adherence of matrix particles to asbestos fibers. To break up large fiber bundles, the suspension was sonicated* according to the following schedule:

Series A,G,H - 15 s at 100 W
Series C,D,E - 30 s at 100 W
Series B,I - 60 s at 100 W

After sonication, the asbestos suspension was transferred to a 240-mL container. The dry matrix material and 50 to 200 mL of deionized water were added. The sample was mixed on a Waring blender for 10 to 15 s at medium speed. The resulting suspension was filtered in a Millipore apparatus (Millipore cellulose ester filter, 0.45 µm pore), transferred to an aluminum boat, and dried overnight at 105° C. The dried sample was sealed in a plastic sample container.

Quality control measures were instituted at several points in the sample preparation phase. Analytical balances were prechecked with a set of weights calibrated against weights traceable to the National Bureau of Standards. Balances were accurate to within 0.3 mg.

Several packets of asbestos fiber and matrix material were selected for reweighing before sample preparation. Differences between first and second weighings were negligible for both asbestos fiber and matrix material and did not introduce significant variations from target weights.

Control samples of matrix material were treated with the sample preparation steps above. The average solubility of the gypsum matrix was 0.2 g/100 mL deionized water amended with SDS. Average matrix weight loss due to drying at 105° C and allowing equilibration at room temperature was 10.8 percent. Corrections for weight loss due to matrix dissolution and drying were used to determine "Actual weight %" in Table 1.

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*Bronson model W185 with 1/2-in. disruptor horn, conical tip.

5.3 DEFINITIONS OF LABORATORY GROUPS

Twenty-six laboratories were asked to perform PLM analyses of the provided samples. Twelve of the twenty-six laboratories have facilities for XRD analysis and were asked to also analyze the samples by XRD. Four laboratories receiving samples chose not to participate in the study. The twenty-two participating laboratories returned a total of thirty PLM reports and six XRD reports. PLM data are summarized in Table 2. XRD data are presented and discussed in Section 7.

Of the 30 sets of PLM results, 19 were produced by following the point count method closely enough to be included in the evaluation of the technique. Three laboratories returned results of analyses by more than one analyst; such results are treated independently. Data not produced by the point count method are included in separate groups.

The reported PLM results were classified by quantitation procedure, as follows. The number of laboratories in each group is in parentheses.

Group P - (Point count) PLM asbestos area percent determinations by the point count method (n = 19).

Group B - (Both) PLM asbestos area percent determinations by laboratories' own methods for laboratories that also provided data by the point count method (n = 6).

Group O - (Other) PLM asbestos area percent determinations by laboratories' own methods for laboratories declining to use the point count method (n = 5).

Data in Group O (other) contributed by different laboratories were not necessarily produced by the same quantitation procedure. Six laboratories that contributed data to Group P (point count) also reported results produced by their own quantitation procedures. This data set is designated Group B (both). Four of the laboratories produced closer estimates of the true weight percents by their own method than by point counting, while the other two laboratories reported closer results by point counting. It is unclear what relationship exists between the Group P and Group B data contributed by any one laboratory. It is possible that an estimate produced by point counting could have influenced a laboratory's own procedure, or vice versa.

TABLE 2. QUANTITATIVE RESULTS OF PLM ANALYSES
(Percent Asbestos by Area)

		Sample series										
		A	B	C	D	E	F	G	H	I	J[c]	K[d]
Laboratory	Group	C[a] 4.9[b]	A 38.8	C 1.2	A 19.4	C 19.4	N 0	A 9.8	A 2.5	C 74.5	C .	C .
PD	P	6	49	5	46	14	0	22	13	50[e]	40	54
PE	P	12	87	4	76	16[e]	0	42	9	93	49	19
PF	P	14	60	9[e]	36	45	0	62	26	77	53	4
PG	P	3	63	0	48	11[e]	0	36	17	65	59	35
PH1	P	1	24	0[e]	17	7	0	5	2	42	50	0
PH2	P	2	26	0	13	10	0	6	2	38[e]	37	35
PJ	P	9[e]	69	7	37	38	0	39	18	60	51	12
PK	P	2	65	2	47	14[e]	0	38	25	55	59	14
PM	P	18.5[e]	61	6	50	53	0	27.5	12	72.5	67	18.5
PN	P	2	20	1[e]	29	14	0	9	5	26	9	0
PP1	P	10[e]	77	11	68	44	0	40	20	84	74	41
PP2	P	2[e]	31	2	28	19	0	13	4	78	54	6
PR	P	18	61	7	61	33	0	52	29	70[e]	35	73
PS	P	18	28	17[e]	18	16	4	15	13	98	70	3
PT	P	4	26	1	14	11	0	9	2	61	.	.
PV	P	9	47	4[e]	34	38	0	10	13	75	53	4
PW1	P	0	49	0	28	10	0	.	.	.	.	.
PW2	P	6	43	0	30	11	0	20	6	48	.	.
PW3	P	3	44	3	39	8	0	26	9	.	.	.
BSS	B	10	35	15	30	20	0	25	10	95	65	4
BNN	B	1.5	75	0	65	30	0	60	40	55	35	0
BPP	B	6	80	4	53	18	0	28	15	65	35	5
BKK	B	5	60	4	40	18	0	35	30	65	60	13
BJJ	B	3	46	7	16	15	0	10	5	50	63	7
BDD	B	4	50	1.5	50	13	0	18	8	48	38	50
01	0	30	50	15	40	60	0	40	40	85	70	35
02	0	70	80	0	60	70	0	50	10	80	80	80
03	0	15	85	15	40	45	5	55	45	85	65	0
04	0	1	35	1	25	10	0	30	3	85	50	1
05	0	8	75	6	42	25	0	25	22	93	60	10

[a] Asbestos type: C = Chrysotile; A = Amosite; N = None

[b] Percent asbestos by weight.

[c] Environmental samples.

[d] Duplicate samples.

[e] Sample series from which duplicate sample (K) was drawn.

5.4 STATISTICAL DEFINITIONS

A method is accurate if it tends to give results that are close to the correct results. A method is precise if it tends to generate values that are close to each other. More specifically, accuracy and precision in the case of a single sample with known weight percent asbestos equal to w, where $w_1, w_2, \ldots, w_n$ are the results of independent analyses, may be defined by the equations:

$$\text{Mean squared error (MSE)} = \frac{1}{n} \sum_{i=1}^{n} (w_i - w)^2 \tag{1}$$

$$\text{Sample variance* } (S^2) = \frac{1}{n} \sum_{i=1}^{n} (w_i - \bar{w})^2 \tag{2}$$

where

w = the true value,

$\bar{w} = \frac{1}{n} \sum_{i=1}^{n} w_i$ is the average of the w_i, and

$i = 1, 2, \ldots, n$.

Letting

$$\text{BIAS} = \text{AVERAGE ERROR} = \bar{w} - w \quad , \tag{3}$$

it follows that

$$\text{MSE} = \text{BIAS}^2 + \text{VARIANCE} \quad . \tag{4}$$

(See Appendix A, Section A.1.) Thus, all questions relating to the accuracy and precision of a method at a given level of asbestos content may be expressed and answered in terms of the average bias and the standard deviation of reported results at that level.

In accord with Eisenhart,[12] it is the opinion of the authors that it is not possible to adequately express accuracy, or overall correctness, in terms of a single numeric measure. At least two measures of the quality of a measurement process are required for its appreciation. It is most natural to separately consider the systematic and the random components of error. The systematic component is bias, and the standard deviation of the random component is often referred to as (im)precision. In the following analysis, therefore, most questions concerning overall accuracy will be addressed in terms of bias and precision.

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*Maximum likelihood estimate; the unbiased estimate (divisor = n-1) was used for actual computations.

5.5 THE RELATIONSHIP BETWEEN AREA PERCENT AND WEIGHT PERCENT ESTIMATES

As indicated in Section 5.1, one of the objectives of the present study is to evaluate precision and accuracy in applying the Tentative Method. Samples were prepared with known weights of asbestos fiber and nonasbestos matrix. Quantitative analysis by PLM results in the estimation of the average percent area occupied by asbestos fiber within examined fields of view. While the area occupied by asbestos within the field of view is obviously dependent on the amount of asbestos present, the estimation of percent area is not a direct measure of the known quantity, percent by weight. To evaluate the accuracy of point counting, therefore, the relationship between the reported estimates of area percent and the known values of weight percent must be investigated.

A microscope field of view is essentially a two-dimensional projection of a portion of the mounted (three-dimensional) sample. The projected area of a solid cylinder (fiber) may be expressed in terms of ℓ^2, where ℓ is some unit of linear measure, e.g., millimeter. The weight (mass) of the cylinder is the product of its volume, in terms of ℓ^3, and its density, in g/ℓ^3. The projected area and the weight of the cylinder are therefore related by some power transformation involving ℓ^2 and ℓ^3. (This is a necessarily simplified version of the more complicated model anticipated, which involved considerations of relative area, relative volume, specific gravity, and geometry of sample constituents.) By extension, projected area percentages of specific particles in a bulk sample might also be related to the particle weight percentages of those particles by a power transformation.[13] In anticipation of this relationship, target weight percents of prepared samples were chosen to be approximately equally spaced on a logarithmic scale.

5.6 THE AREA/WEIGHT RELATIONSHIP IN POINT COUNT DATA

Group P (point count) data are presented in Figure 2. The range of the values reported for each sample series is apparent. For example, reported values for percent asbestos vary from 13 percent to 76 percent for samples containing 19.4 percent amosite by weight, and from 26 percent to 98 percent for samples containing 74.5 percent chrysotile by weight. Figures 3a and 3b present Group P (point count) data for chrysotile and amosite separately. Comparison of the two figures reveals a difference between the ways in which chrysotile and amosite data are related to the A=W line. This suggests that the area/weight relationship is different for the two asbestos types. The same data are presented in natural logarithmic coordinates in Figures 4a and 4b. The increased linearity of the data in natural log coordinates is consistent with the preliminary assumption that a power function is involved in the area/weight relationship.

Linear regression in logarithmic coordinates* was used to study the relation between area percents A as measured by point counting and nominal weight percents W. A standard equation for the power transformation model was used.

$$\text{If} \quad A = bW^c \ ,$$

$$\text{then} \quad \ln(A) = c \ln(W) + \ln(b) \ . \qquad (5)$$

The relation (5) was fitted to the data of Group P (point count) using the General Linear Models procedure of the Statistical Analysis System, a preprogrammed statistical procedures package. The slope (c) and intercept (b) were each allowed to vary with laboratory (PD, PE, etc.) as well as with asbestos type. This is equivalent to fitting individual lines to each laboratory's data separately for chrysotile and amosite. The results of the regression are presented in Appendix A, Section A.2. The results of the analysis support the following conclusions.

1. There is a significant difference between the area/weight relationships for the two types of asbestos. (The variation is best demonstrated in Figures 3a and 3b, plotted in original coordinates, which show that lines fit to amosite and chryso-

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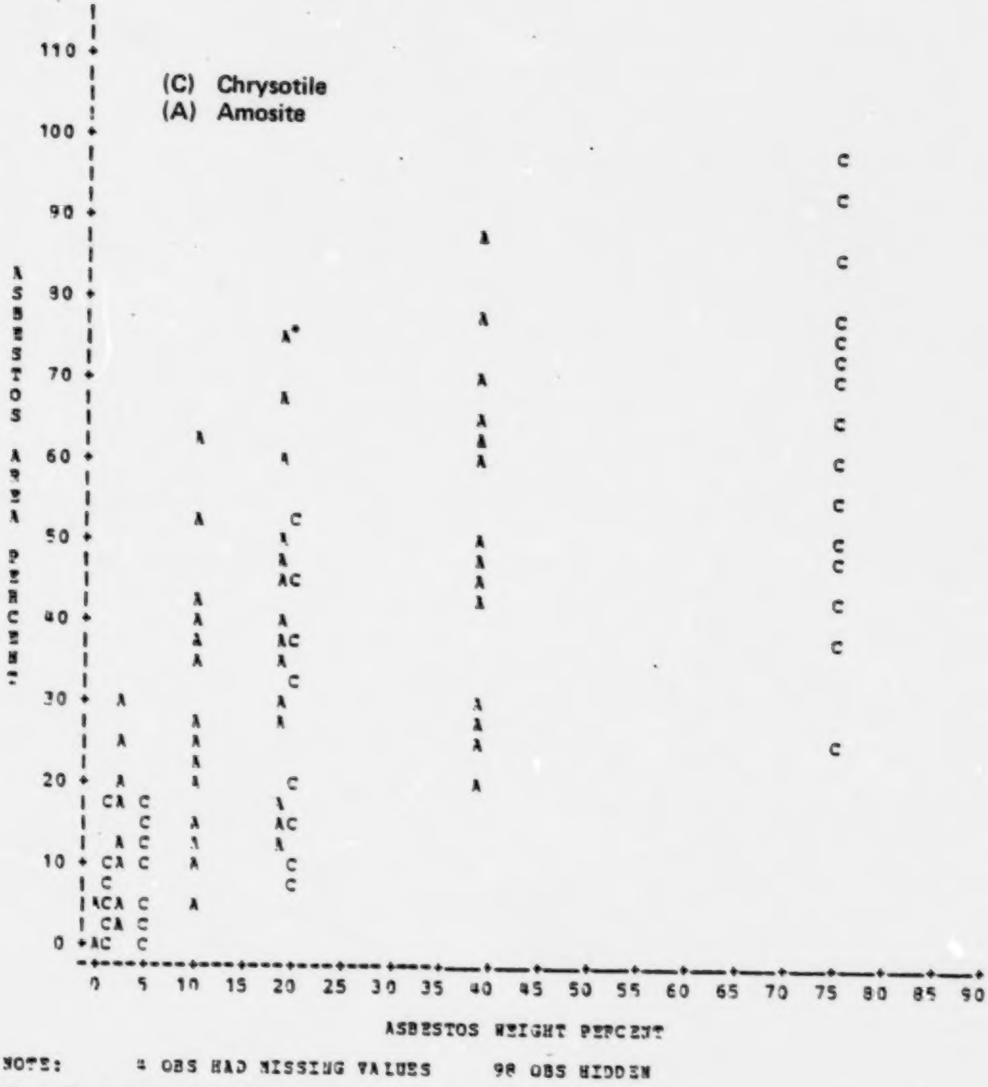
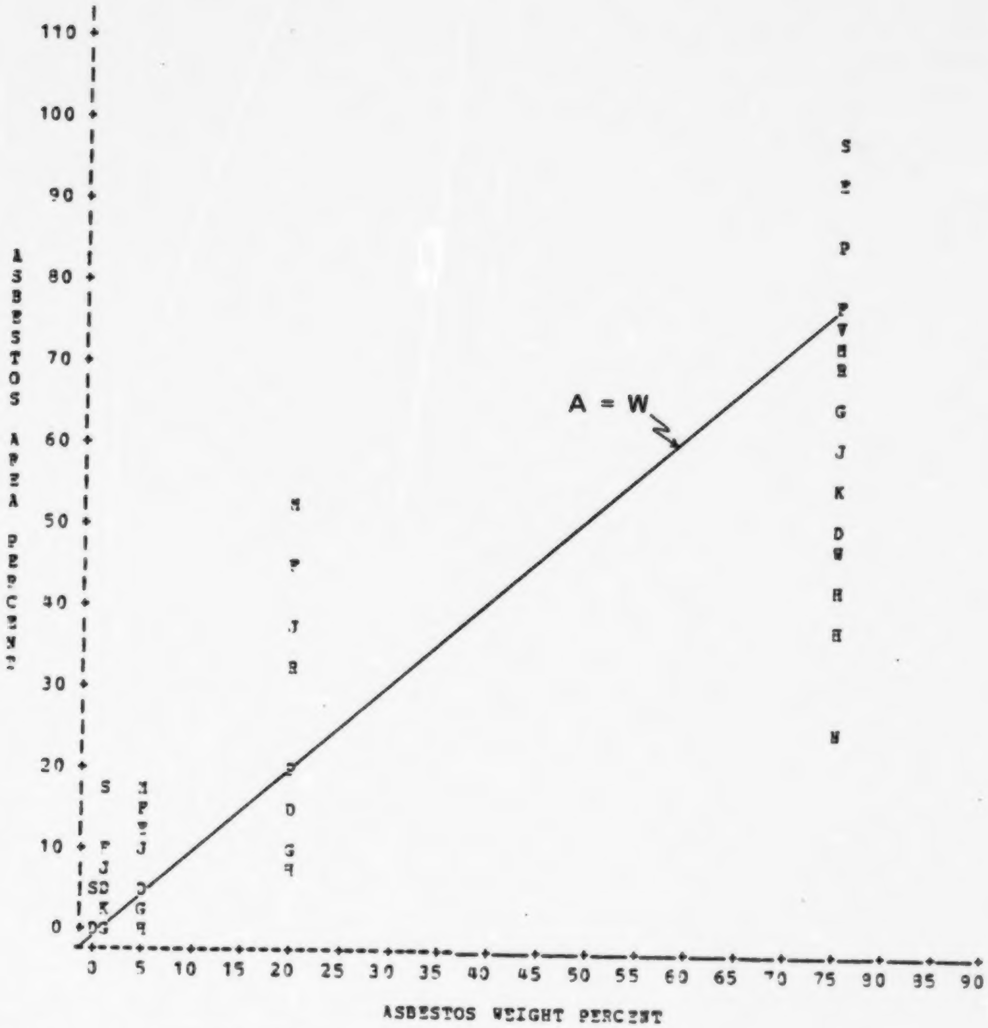
*This and all subsequent uses of logarithms or logarithmic coordinates refer to natural (base e) logarithms.



*Series D is assigned a weight % = 19;
Series E is assigned a weight % = 20.

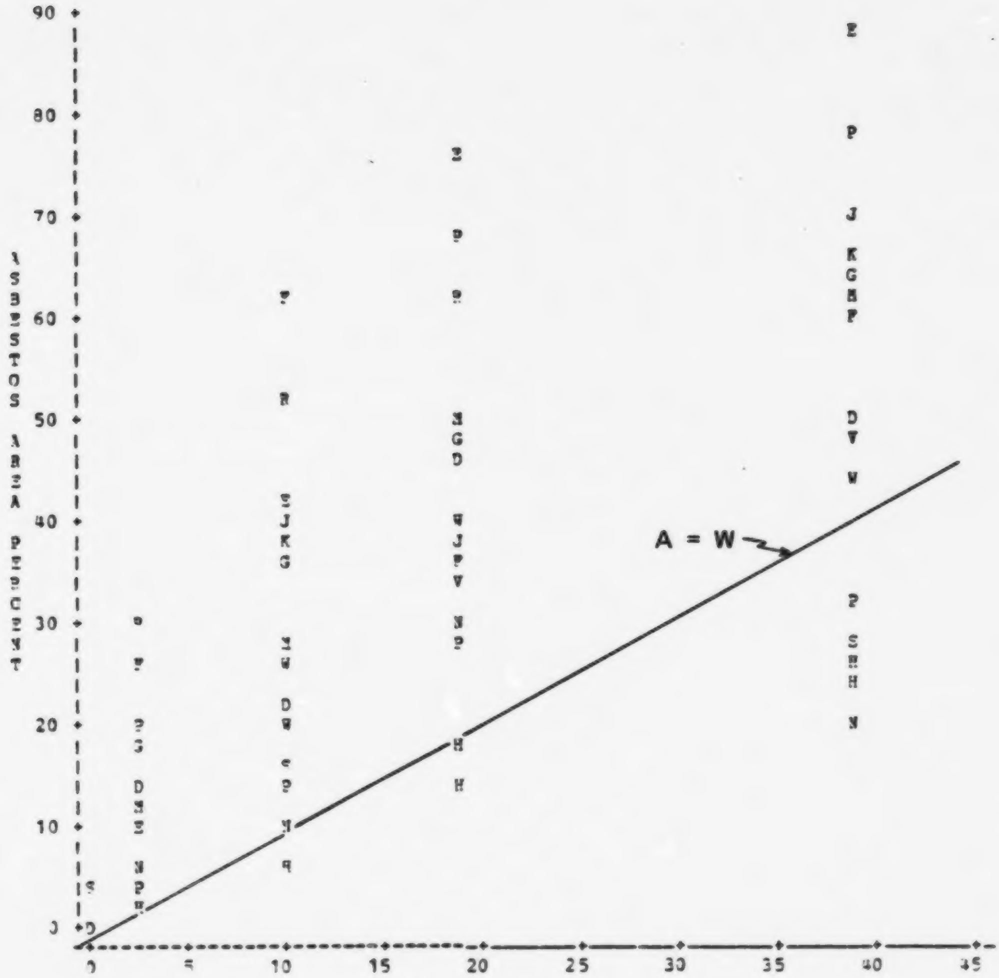
Figure 2. Group P data, by sample series.



NOTE: 2 OBS HAD MISSING VALUES 55 OBS HIDDEN

(Letters refer to the laboratory contributing the data point.)

Figure 3a. Group P data for samples containing chrysotile.



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NOTE:      [illegible] OBS HAD MISSING VALUES     39 OBS HIDDEN
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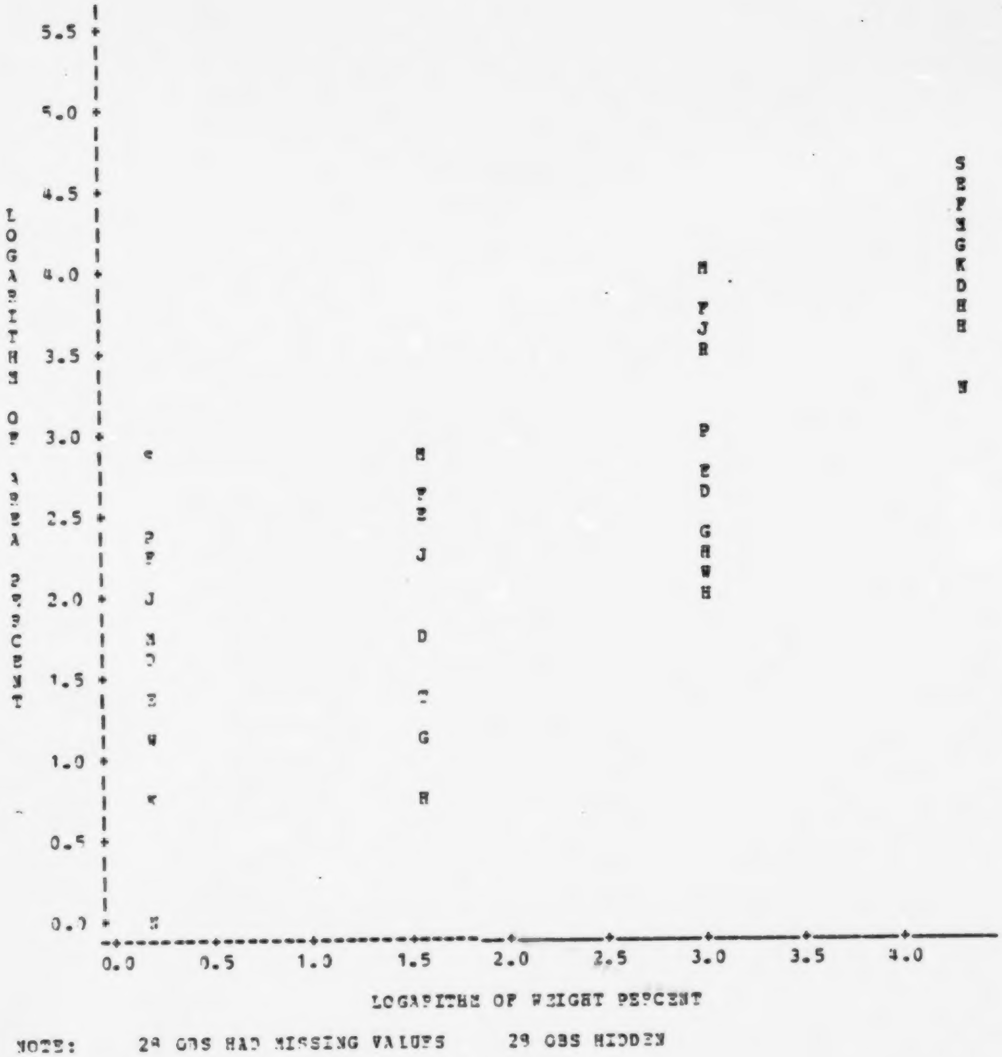
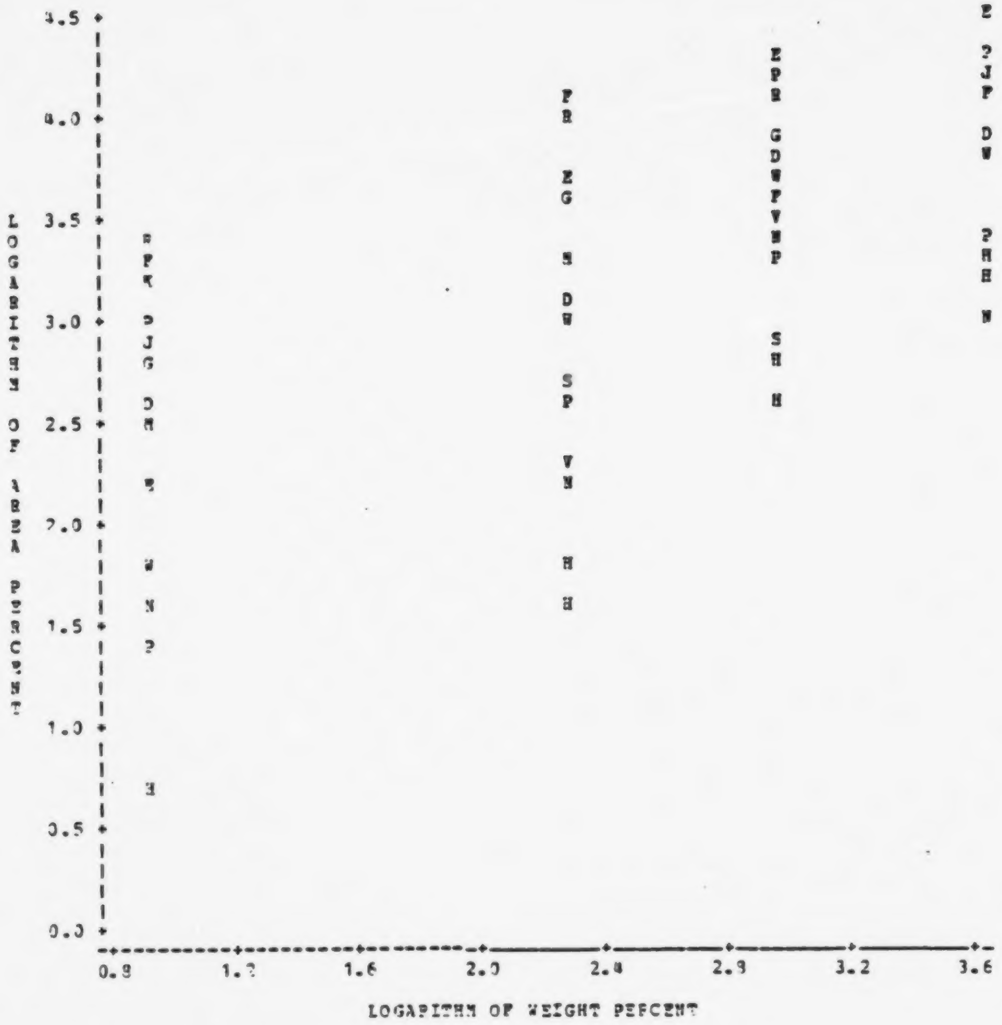
(Letters refer to the laboratory contributing the data point.)

Figure 3b. Group P data for samples containing amosite.



(Letters refer to the laboratory contributing the data point.)

Figure 4a. Natural logarithms of Group P data for samples containing chrysotile.



NOTE: 21 OBS HAD MISSING VALUES 25 OBS HIDDEN

(Letters refer to the laboratory contributing the data point.)

Figure 4b. Natural logarithms of Group P data for samples containing amosite.

tile samples separately would have different slopes and intercepts. The effect is present but somewhat less apparent in Figures 4a and 4b.)

2. There are significant differences between the area/weight relationships in data submitted by different laboratories. (The between-laboratory variation is apparent in Figures 4a and 4b. Laboratories H and N tend to report the lowest values and laboratory F tends to report high values.)

3. The between-laboratory and asbestos-type effects are not independent. [All second-order interactions are significant (see Appendix A, Section A.2). Previous tests had shown that third-order interactions are not significant.]

The importance of individually calibrating laboratories can also be seen when considering precision. Precision more than doubles (standard deviation decreases by more than half) when laboratory effects are incorporated into the appropriate regression (results not shown). Equal variances were assumed for all laboratories or groups. The assumption is known to be false, so this comparison is presented as a descriptive rather than an inferential statistic.

Operationally, the above conclusions suggest that gains in accuracy of the Group P data (and, by extension, of future PLM analyses by the point count method) may be made by individually calibrating laboratories. Further gains may be made by calibrating separately for chrysotile and amosite. Similar tests indicate that the same conclusions hold for Group B (both) and for Group O (other), although the dependence on asbestos type is marginal for Group O. "Calibration" does not necessarily mean providing calibration coefficients to all laboratories. It is meant to imply any means by which laboratory-specific adjustments of quantitative results can be made. Two ways of accomplishing such an adjustment are a round-robin analysis program and the development and distribution of "standard" samples. Laboratories provided with well-characterized samples are likely to modify and improve their techniques until their quantitative results consistently correspond with reference values.

The conclusions stated above must be taken into account in the data analysis for evaluation of the Tentative Method. It is of interest to examine the performance of the method in two contexts: (1) as PLM is currently used, regarding reported area percent as a direct estimate of weight percent; and (2) allowing adjustments of the data that could reasonably be expected, such as calibrating for the effects observed above by transforming area percent estimates to predicted weight percents. For this reason, the main analysis of the PLM data will be presented in three parts. First, accuracy (bias) will be examined assuming the area percent results are estimates of weight percent without any adjustments. Second, the precision of the PLM methods will also be considered without adjustments of the data. Finally, accuracy and precision will again be considered after transforming the area percent estimates to predicted weight percent values.

SECTION 6

METHOD EVALUATION: POLARIZED LIGHT MICROSCOPY

6.1 BIAS OF THE PLM DATA

Group means and standard deviations for sample series A through J are summarized in Table 3. Recall that Group P (point count) is data produced by point counting, Group O (other) is data produced by laboratories' own methods, and Group B (both) is data produced by laboratories' own methods for those laboratories that also contributed point count data. Note in Table 3 that for six of nine cases the mean of the point count group (MP) is closer to the nominal weight than the mean of Group B (MB). This is not a significant difference, and it appears that Groups P and B are comparably biased. Individual t-tests for differences between MP and MB performed for each sample are not significant. A more powerful test for differences between biases using regression analysis also supports the conclusion that Groups P and B are comparably biased (see Appendix A, Section A.3).

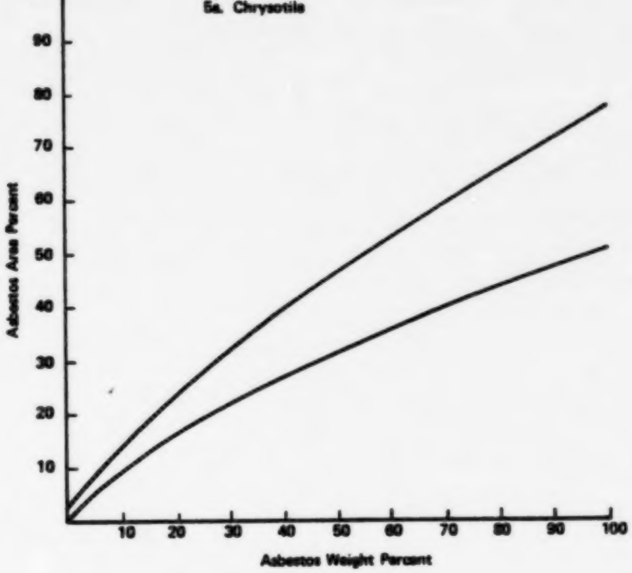
Note also in Table 3 that means of Group O results are consistently higher than those of Groups P and B. Sign tests suffice to show that Group O is significantly more biased than Groups P and B. Group O means were further from the nominal weight than Group P means on all nine prepared samples; the probability of a result this extreme occurring by chance is $2(\tfrac{1}{2}^{9}) = 0.004$ (two-sided test). Group O was further from the loaded weight than Group B on eight of the nine samples; the corresponding probability is $2[(1+9)/2^{9}] = 0.04$ (two-sided test). Group O is the furthest from the loaded weight of the three PLM groups on eight of the nine samples, with probability $2[1/3^{9} + 9 \cdot 2/3^{9}] < 0.002$ (two-sided test). The difference in bias between Groups O and P is confirmed by regression analysis (see Appendix A, Section A.3).

The 90-percent confidence intervals for Group P (point count) data for chrysotile and amosite samples are presented in Figures 5a and 5b, respectively. Calculations were performed on log-transformed data and the results then exponentiated. The procedure used accounts for unequal variance of

TABLE 3. MEANS AND STANDARD DEVIATIONS OF REPORTED PLM RESULTS, BY GROUP (P, B, O)

(percent asbestos by area)

Series	Type	Weight %	Means MP	Means MB	Means MO	Standard deviations SP	Standard deviations SB	Standard deviations SO
C	Chrysotile	1.2	4.2	5.3	7.4	4.5	5.3	7.3
A	Chrysotile	4.9	7.3	4.9	24.8	6.3	2.9	27.5
E	Chrysotile	19.4	21.7	19.0	42.0	14.8	5.9	24.6
I	Chrysotile	74.5	64.3	63.0	85.6	19.6	17.3	4.7
H	Amosite	2.5	12.5	18.0	24.0	8.6	13.9	18.3
G	Amosite	9.8	26.2	29.3	40.0	16.9	17.3	12.7
D	Amosite	19.4	37.8	42.3	41.4	17.7	17.5	12.4
B	Amosite	38.8	48.9	57.7	65.0	19.5	17.4	21.5
F	None	0.0	0.2	0.0	1.0	0.9	0.0	2.2
J	Environmental	-	50.7	49.3	65.0	16.1	14.7	11.2


5a. Chrysotile

5b. Amosite

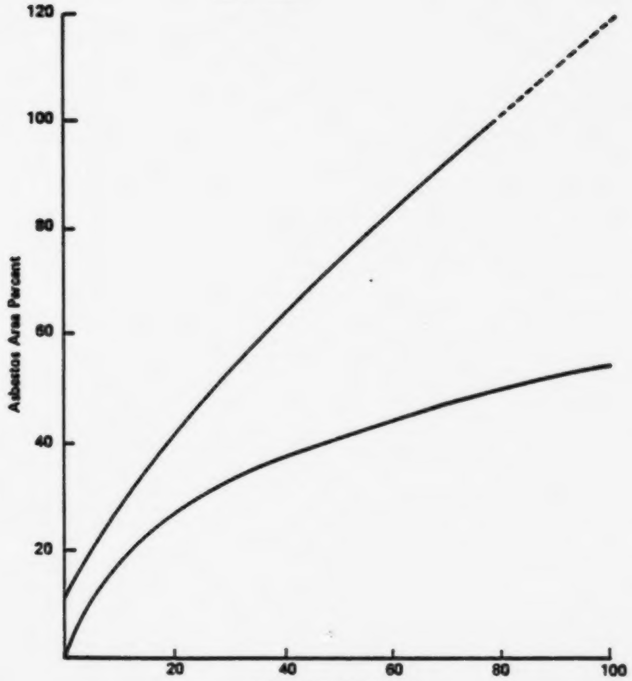


Figure 5. Ninety percent confidence intervals for means of Group P data.

sample series containing different weight percents of asbestos;[14] [15] the confidence statement holds simultaneously at all levels of asbestos. The figures should be interpreted as follows. For a sample containing 20 percent chrysotile by weight ($W_C = 20$), the mean estimate of relative area by point counting will be between approximately 16 and 23 percent, with a probability of 0.90. Similarly, for $W_C = 50$, 90 percent of the means of point count analyses will be between approximately 31 and 44 percent. The same relationships demonstrate a positive bias for Group P analysis of samples containing amosite. For a sample with $W_A = 20$, the 90-percent confidence limits are approximately 27 and 38 percent; for $W_A = 50$, the limits are approximately 41 and 71 percent.

Using the midpoints of the confidence intervals, the average percent bias of Group P (point count) analyses was estimated at several weight percent levels. These are presented in Table 4 and Figure 6. The percent bias varies with weight percent of asbestos similarly for amosite and chrysotile samples. Point counting has a greater positive bias on amosite samples than on chrysotile samples and, in fact, underestimates asbestos content in samples containing more than about 18 percent chrysotile by weight.

6.2 PRECISION OF THE PLM DATA

Precision will be evaluated with an approach based on the standard deviation of reported results. The standard deviation is the most common measure of variation or imprecision. If one group or method is systematically more variable than another, the trend may be evident in a plot such as Figure 7, in which group standard deviations (SP, SB, SO in Table 3) are related to nominal weight percentages. Group P sample standard deviations are larger than those of Group B on six of nine samples, but are reasonably comparable on all except sample E. Group O standard deviations exceed those of Groups P and B on the four samples with less than 5 percent asbestos, suggesting that Group O data are less precise on samples in this range.

The standard deviation of reported PLM data increases as the weight percent of asbestos increases for all groups; i.e., variance is directly related to the percent asbestos present. Figures 8a and 8b present the relationship between standard deviation (SP) and weight percent (W) or mean reported area percent (MP), respectively, for Group P. Data points conform

TABLE 4. AVERAGE PERCENT BIAS OF GROUP P DATA

Asbestos type	Weight percent W	CI midpoint X	% Bias = $\frac{X-W}{W} \times 100$
Chrysotile	10	11.85	18.5
	20	19.60	-2.0
	50	37.90	-24.2
Amosite	10	21.85	118.5
	20	32.35	61.8
	50	56.05	12.1

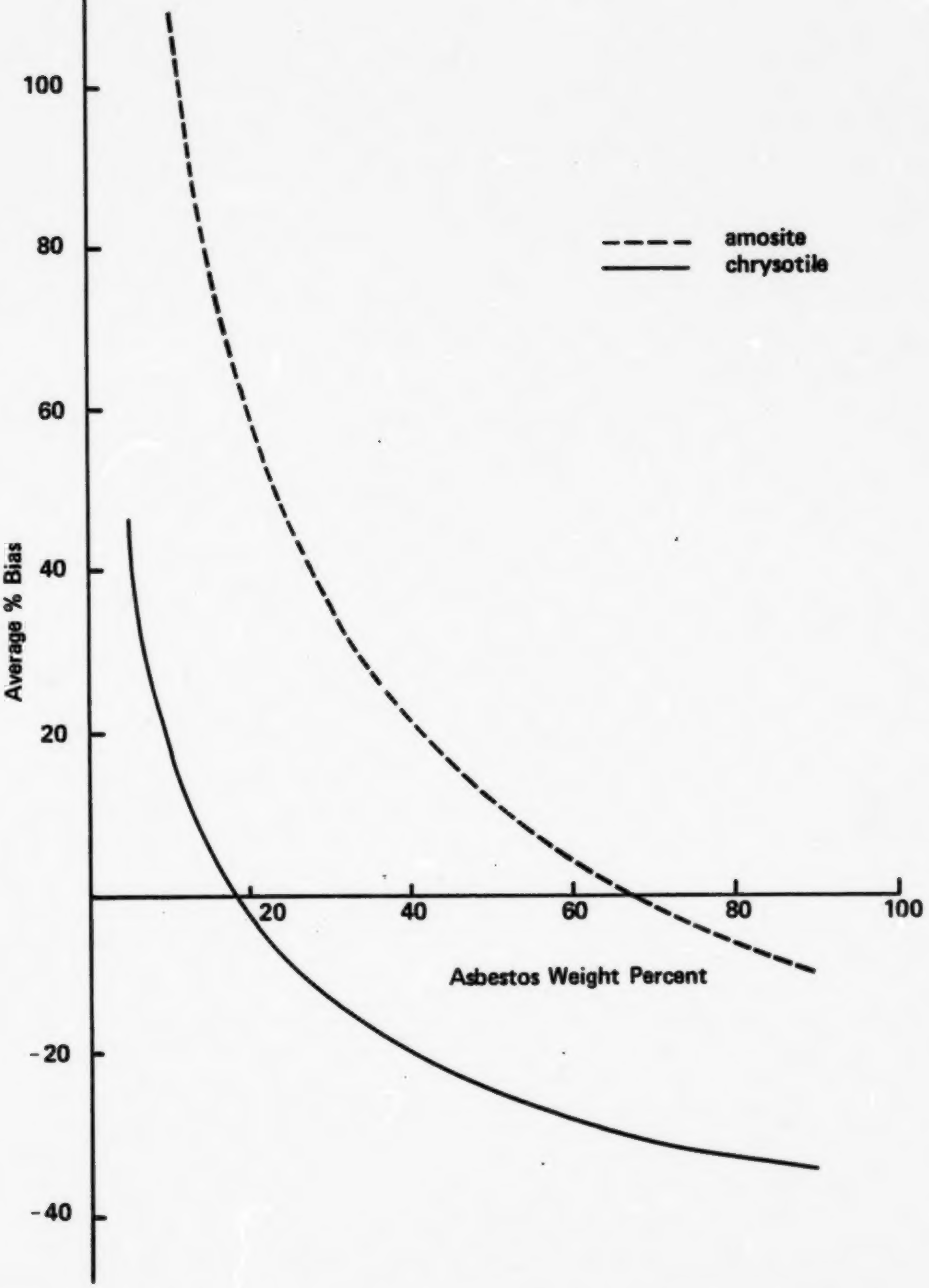


Figure 6. Average percent bias of Group P data.

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PLOT OF SP*WEIGHT    SYMBOL USED IS P
PLOT OF SB*WEIGHT    SYMBOL USED IS B
PLOT OF SO*WEIGHT    SYMBOL USED IS O
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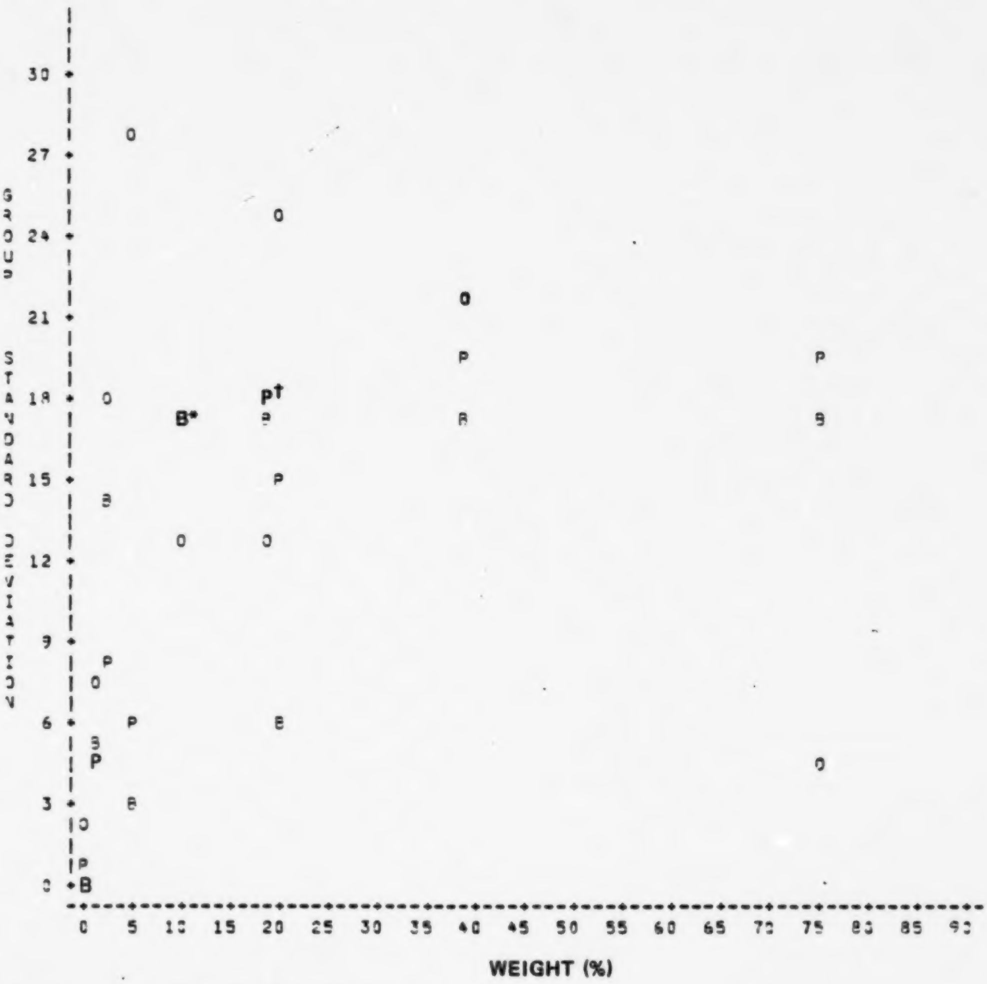

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NOTE:      4 OBS HAD MISSING VALUES
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*P and B have the same value.

†Series D is assigned a weight % = 19;
Series E is assigned a weight % = 20.

Figure 7. Group standard deviations.

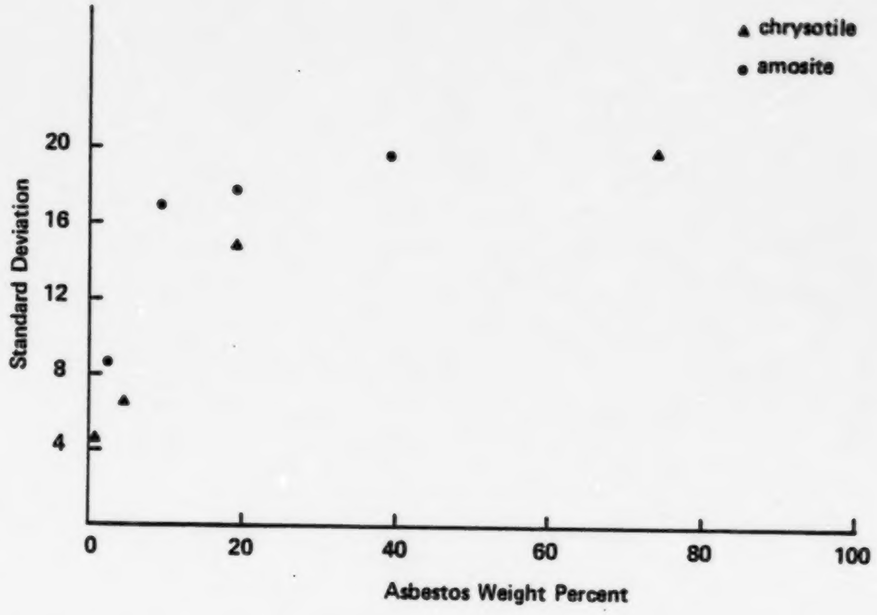


Figure 8a. Group P standard deviation vs. asbestos weight percent.

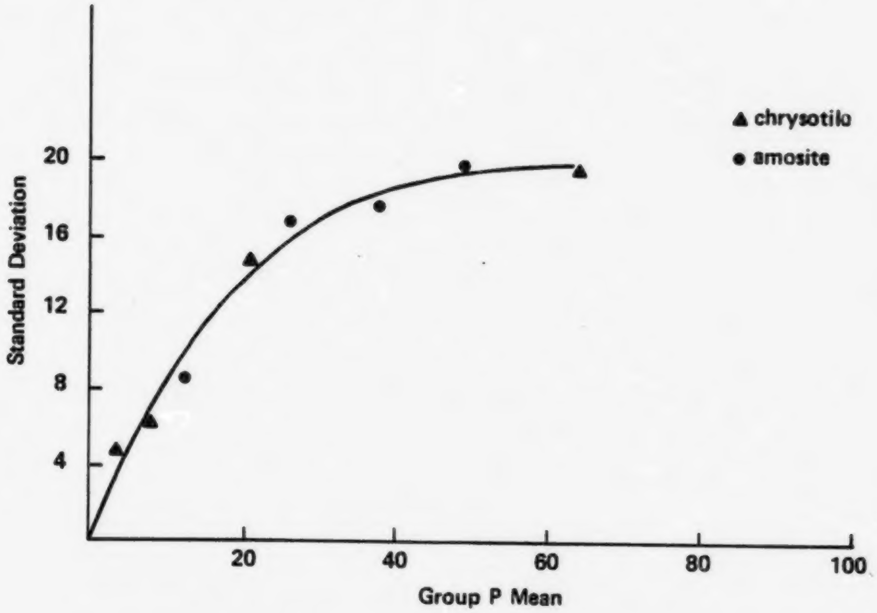


Figure 8b. Group P standard deviation vs. Group P mean.

more closely to a single curve in Figure 8b. Regression of ln (SP) on ln (W) ($R^2 = 0.81$) and on ln (MP) ($R^2 = 0.96$) suggests that the variance is more systematically related to the reported area percent asbestos than to the known weight percent asbestos.

The suggested difference in precision between Group O (other) and Groups P (point count) and B (both) may be due to the larger bias of Group O results (Section 6.1). Because variance is directly related to reported area percent, larger standard deviations may result simply from the Group O tendency to report higher values. Differences between groups with respect to precision were investigated with regression analysis, allowing information to be combined from samples loaded at different weight percentages. The results of the regression (see Appendix A, Section A.4) indicate that, when differences in bias between groups are accounted for, Groups P, B, and O are not significantly different with respect to precision.

Precision is sometimes expressed as the percent relative standard deviation or coefficient of variation (CV = 100 SP/MP). CV is related to Group P means in Figure 9. The CV is less than 100 percent on samples with more than approximately 6 percent asbestos by area and less than 50 percent on samples with more than approximately 32 percent asbestos by area. At a mean reported value (MP) of 10 percent asbestos, CV ≅ 79 percent; at MP = 20 percent, CV ≅ 61 percent; at MP = 50 percent, CV ≅ 41 percent.

6.3 ACCURACY AND PRECISION, AFTER DATA TRANSFORMATION

As stated earlier, it is of interest to evaluate the accuracy of the PLM methods after adjusting for the relationship between reported area percent and the known weight percent of the samples. This will allow not only a better understanding of what reported PLM data mean, but will also indicate what improvements might be made in data quality by adjusting PLM area percent estimates to better represent weight percent. Such an adjustment of the data generated in the present study is possible using parameters similar to those determined in the regressions discussed in Section 5.5. This adjustment formally applies only to the samples and laboratories in this study and would be questionable for other laboratories and other samples of different composition. Further study would be required to deter-

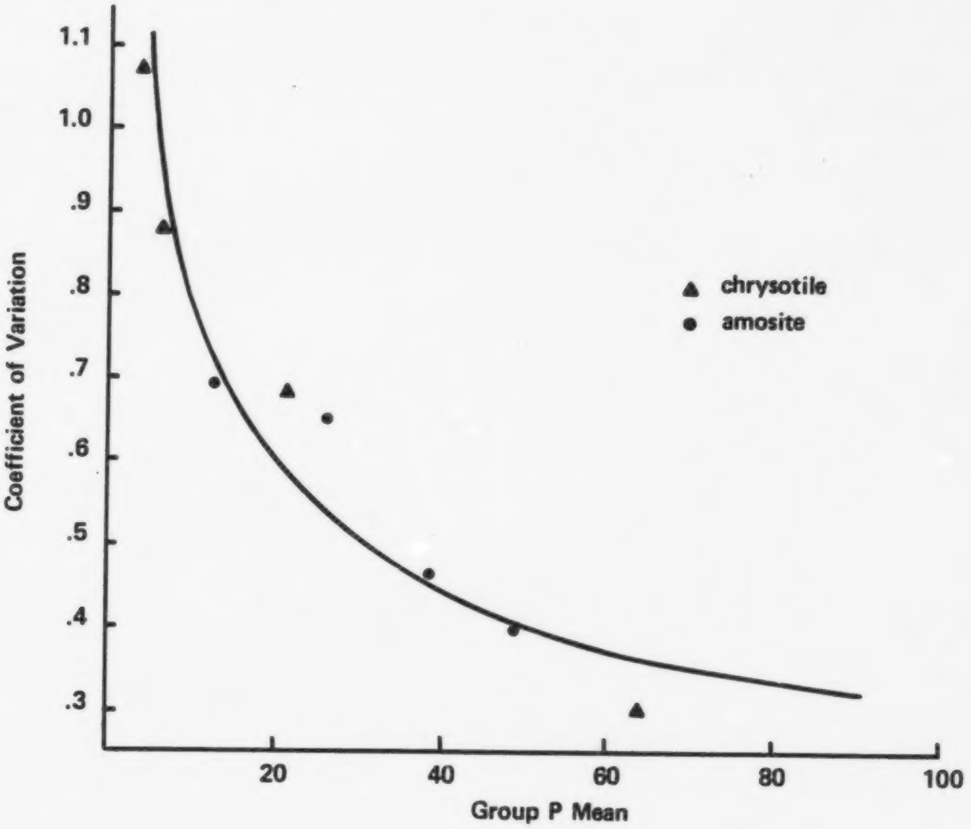


Figure 9. Coefficient of variation of Group P data.

mine if a small family of functions, specific for asbestos and matrix type, could be used generally to adjust PLM data to more adequately represent percent asbestos by weight.

Groups P, B, and O area-percent data (A) were adjusted for laboratory and asbestos-type effects to yield predicted weight percents ($\hat{W}$) for each individual result. Means and standard deviations of $\hat{W}$ were then computed for each group ($\hat{MP}$, $\hat{SP}$, etc.). These are presented in Table 5. Details of the transformation may be found in Appendix A, Section A.5.

The accuracy of predicted weights ($\hat{W}$) was evaluated by determining the average percent absolute error (ERROR ($\hat{W}$)), or the average difference between $\hat{W}$ and W. This is calculated as

$$\text{ERROR } (\hat{W}) = \frac{1}{n_i} \sum_{j=1}^{n_i} \frac{\hat{W}_{ij} - W_i}{W_i} \; 100 \; \%$$

where j = 1, . . . , and n_i indexes the reported analyses for each group on the i^{th} sample. ERROR ($\hat{W}$) is then compared to the same quantity computed for the untreated data,

$$\text{ERROR } (A) = \frac{1}{n_i} \sum_{j=1}^{n_i} \frac{A_{ij} - W_i}{W_i} \; 100\% \; .$$

ERROR (A) and ERROR ($\hat{W}$) are tabulated by group in Table 6.

The most obvious and expected result in comparing the average percent absolute errors of treated and untreated data is the considerable gain in accuracy (reduction of error) that results from the transformation $A \rightarrow \hat{W}$. For example, the average Group P inaccuracy for unadjusted data on samples containing asbestos is 155 percent. After transformation, the inaccuracy drops to 31 percent, or only one-fifth of the original.

For Groups P and B the percent error is fairly stable over the five samples between 2.5 and 20 percent asbestos by weight. The average of ERROR ($\hat{W}$) for these five samples is 30 (±5) percent for Group P and 32 (±11) percent for Group B. For Group O (other), the corresponding values are more variable and tend to indicate less accuracy. The Group O average ERROR ($\hat{W}$) for the same five samples is 63 (±35) percent.

TABLE 5. MEANS AND STANDARD DEVIATIONS OF PREDICTED WEIGHT ($\hat{W}$), BY GROUP (P, B, O)

Series	Type	Weight %	Means $\hat{MP}$	Means $\hat{MB}$	Means $\hat{MO}$	Standard deviations $\hat{SP}$	Standard deviations $\hat{SB}$	Standard deviations $\hat{SO}$
C	Chrysotile	1.2	2.1	3.4	1.9	1.1	2.6	0.5
A	Chrysotile	4.9	4.3	3.4	4.7	1.6	1.2	3.4
E	Chrysotile	19.4	20.5	18.1	17.8	9.1	11.5	8.6
I	Chrysotile	74.5	72.9	73.0	74.0	3.7	6.0	2.7
H	Amosite	2.5	3.1	2.8	5.5	1.2	0.3	3.3
G	Amosite	9.8	11.1	9.7	13.9	4.9	4.4	7.4
D	Amosite	19.4	21.7	19.0	14.3	6.4	7.3	6.6
B	Amosite	38.8	33.9	36.6	35.3	5.8	5.0	6.1

TABLE 6. AVERAGE PERCENT ABSOLUTE ERROR: UNADJUSTED VS. TRANSFORMED PLM DATA, BY GROUP (P, B, O)

Series	Type	Weight %	Group P		Group B		Group O	
			Error (A)	Error ($\hat{W}$)	Error (A)	Error ($\hat{W}$)	Error (A)	Error ($\hat{W}$)
C	Chrysotile	1.2	313.9	75.0	370.8	179.6	563.3	62.2
A	Chrysotile	4.9	105.1	28.4	42.5	36.0	438.0	56.7
E	Chrysotile	19.4	60.5	34.0	21.7	44.0	130.0	36.0
I	Chrysotile	74.5	27.2	3.2	24.6	4.1	14.9	2.3
H	Amosite	2.5	406.7	23.7	620.0	13.5	860.0	120.5
G	Amosite	9.8	178.9	34.7	199.3	37.6	308.2	68.2
D	Amosite	19.4	106.9	30.9	128.1	29.4	117.9	33.2
B	Amosite	38.8	47.3	14.3	51.9	10.3	71.4	12.8

After variance due to laboratory and asbestos-type effects is removed by the above transformation, residual variance is reflected in dispersion about the regression line of $\hat{W}$ on W. In this context, mean squared error about the regression line is a measure of precision. The analyses were performed in log coordinates since the correlations obtained typically exceeded R = 0.99. The basic result is that Group P is significantly more precise than Groups B and O after between-laboratory variance is removed. Specifically, allowing the slope (c) and intercept (d) to vary with laboratory and asbestos type, the Group P mean squared error (MSE(P) = 0.123) was less than that of Groups B and O (MSE(B) = 0.264, MSE(O) = 0.226). The differences between Group P and Groups B and O are significant at the 0.01 and 0.05 level, respectively, by standard two-sided F tests.

The above analysis shows that, if laboratories had access to information with which they could calibrate their results (according to the area-weight relationship for each laboratory and asbestos type), considerable gains in accuracy and precision of results could be achieved. The gains would be greater for laboratories using the point counting quantitation procedure than for laboratories using alternative procedures.

6.4 ESTIMATION OF WITHIN-ANALYST VARIANCE

A duplicate sample was included among the samples sent to each laboratory in an effort to collect preliminary data for estimating within-laboratory variance. Since data supplied by different analysts from the same laboratory are being treated independently, what will be estimated is actually within-analyst variance. More than one duplicate sample per analyst would be required to adequately characterize this component of total variance, but a rough estimate may be gained from the present information.

Samples from the chrysotile series (C, A, E, and I) were reassigned to sample series K and then distributed. Returned results included analyses of five duplicate samples from Series C, four from Series A, and three each from Series E and I, as summarized in Table 7.

On 11 of the 15 reported pairs, the duplicate variance estimate was less than 25 percent of the total variance estimate for the corresponding sample series. Each within-sample median variance was less than 25 percent of the total variance for the sample. It therefore appears that within-

TABLE 7. ANALYSIS OF DUPLICATE SAMPLES, GROUP P

Series	Type	Weight %	LAB[a]	Results	Std. dev. S	Median S (S^2)	Sample S[b] (S^2)
C	Chrysotile	1.2	PH1	0, 0	0		
			PV	4, 4	0		
			PN	1, 0	0.7	0.7	4.5
			PF	9, 4	3.5	(0.5)	(20.3)
			PS	17, 3	9.9		
A	Chrysotile	4.9	PM	18.5, 18.5	0		
			PJ	9, 12	2.1	2.5	6.3
			PP2	2, 6	2.8	(6.3)	(39.7)
			PP1	10, 41	21.9		
E	Chrysotile	19.4	PK	14, 14	0		
			PE	16, 19	2.1	2.1	14.8
			PG	11, 35	17	(4.4)	(219.0)
I	Chrysotile	74.5	PR	70, 73	2.1		
			PH2	38, 35	2.1	2.1	19.6
			PD	50, 54	2.8	(4.4)	(384.2)

[a] See Table 2.

[b] See Table 4.

analyst variance probably contributes less than 25 percent of the total variance, which again implies that most of the variance in the point count data (Group P) is due to between-laboratory differences. This is not surprising and is consistent with the already noted doubling of precision that results from calibration of individual laboratories (See Section 5.6).

6.5 FALSE POSITIVES AND NEGATIVES FOR POINT COUNT DATA

One of the important characteristics of the point count procedure to be evaluated is the likelihood of its generating false positives and false negatives. A false positive occurs when an analyst reports asbestos present in a sample that does not contain asbestos. A false negative occurs when an analyst reports no asbestos present in an asbestos-containing sample.

Group P data for the 1.2 percent chrysotile samples (Series C) included five false negatives out of a total of 19 analyses. Two of the false negatives were reported by analysts in the same laboratory (PH1, PH2).

Group P data for the 4.9 percent chrysotile samples (Series A) contained one false negative in 19 analyses. The same laboratory reported one of the false negatives on the 1.2 percent samples. No false negatives were reported for any samples containing amosite or more than 5 percent chrysotile.

One false positive was reported for the blank samples (Series F) in Group P. Laboratory S reported 4 percent tremolite-actinolite asbestos present. Since no other laboratories reported tremolite or actinolite asbestos in any samples, and Laboratory S reported it only for sample F, the false positive is probably due to contamination.

The point counting procedure involves counting 400 points on eight subsamples of the material being analyzed. For the false negatives discussed above, laboratories scored three or fewer points for asbestos fiber, and thus less than 1 percent (4/400) asbestos was reported. The Tentative Method procedure supplied to the laboratories included the statement, "if seven or fewer of 400 non-empty points are scored for asbestos fiber, report less than one percent asbestos." This provision was based on regarding data as a test of the hypothesis that the percent asbestos in a sample is less than or equal to one. A Poisson distribution of the results of repeated analysis of low percentage samples was assumed. At present, however, data are not sufficient to determine whether repeated analysis of "real-world" samples fits the Poisson model. Additionally, it is more appropriate to the normal use of reported data to regard it as estimating percentage rather than testing a specific hypothesis. It is therefore recommended that the simple arithmetic percentage ([points scored for asbestos ÷ total points counted] × 100) be used at all levels until further data may justify the Poisson assumption and/or a specific percent criterion is established. The simple arithmetic percentage was used for the determination of false negatives in this study.

The one false negative reported for point counting analysis of the 4.9 percent chrysotile sample represents a false negative probability of 0.05 (1/19). This estimate formally applies only to the present study; analysis of "real-world" samples may be subject to a higher rate. Current EPA guidance recommends at least three samples be taken from each "sampling area," defined as "any area, whether contiguous or not . . . which contains friable material that is homogeneous in texture and appearance."[16] For this study, the probability of obtaining three false negatives on the 4.9 percent chrysotile sample was 0.05^3, or less than 0.001. Taking 0.10 as a conservative estimate of the rate of false negatives for samples containing 5 percent asbestos, the probability of obtaining false negatives on all three samples, if they each contain at least 5 percent asbestos, is 0.10^3 or 0.001. If the false negative rate was even as high as 0.30, then the probability of false negatives on all three samples would still be only 0.027.

The counting of 400 points provides a good estimate of the area percent of asbestos within the examined fields of view. The counting of four times this number (1,600 points) would be required to double the precision of the estimate. The accuracy of point count data, especially in samples containing small amounts of asbestos, is strongly dependent on factors other than the number of points counted. These include representative sampling of the bulk material, adequate sample preparation, and uniform dispersal of the sample material on slides. Variation associated with these sources greatly affects the lower detection limit of the method and is likely to be more responsible for the occurrence of false negatives than is the actual point counting procedure. Further study is required (see Section 3.1) to determine what improvements and standardization can be achieved in these aspects of the current methodology.

6.6 OPERATING CHARACTERISTIC CURVES

The evaluation of false negatives is complicated by the area-weight relationship as discussed previously. The quantity of interest is not the quantity that is being directly measured. Therefore, it is relevant to evaluate the error rates of the point count method after transforming the data to predicted weights ($A \rightarrow \hat{W}$; see Section 6.3). The evaluation will use a criterion other than false positives and negatives.

Figure 10 presents the operating characteristic (OC) curves for an idealized error-free method and a hypothetical very accurate method. The proportion of laboratories reporting less than level X of asbestos in a given sample is plotted against the known weight percent of asbestos in the sample. For samples with less than X percent asbestos, the decision is correct if and only if a laboratory's result is also below X. It is desirable that the OC curve remain close to 1.0 below the decision criterion X and drop rapidly to 0 as the threshold X is crossed. This is illustrated by the curve in Figure 10. For samples containing less than X percent asbestos, a majority of laboratories report less than X percent present; for samples containing more than X percent asbestos, a minority of laboratories report less than X percent present; for samples containing exactly X percent asbestos, one-half of the laboratories report less than X percent present.

Figure 11 presents the OC curves for the adjusted point count data at four different criteria levels: Figure 11a, X = 1 percent; 11b, X = 2 percent; 11c, X = 5 percent; 11d, X = 7 percent. The proportion of laboratories reporting values yielding predicted weights ($\hat{W}$) less than X is plotted against the known weight percent of asbestos in the sample. Thus, in Figure 11b, more than 60 percent of the $\hat{W}$ were less than 2 percent for the 1.2 percent chrysotile sample (Series C), approximately 40 percent of the $\hat{W}$ were less than 2 percent for the 4.9 percent chrysotile sample (Series A), and none of the $\hat{W}$ were less than 2 percent for the 9.8 percent amosite sample (Series G).

Figures 11a and 11b suggest that laboratories are not able to reliably distinguish between samples containing <1 percent and >1 percent asbestos or between samples containing <2 percent and >2 percent asbestos. The performance of the method improves at X = 5 and is better still at X = 7. Figure 11d suggests that laboratories, after calibration, are able to reliably decide whether a particular sample contains <7 percent or >7 percent asbestos.

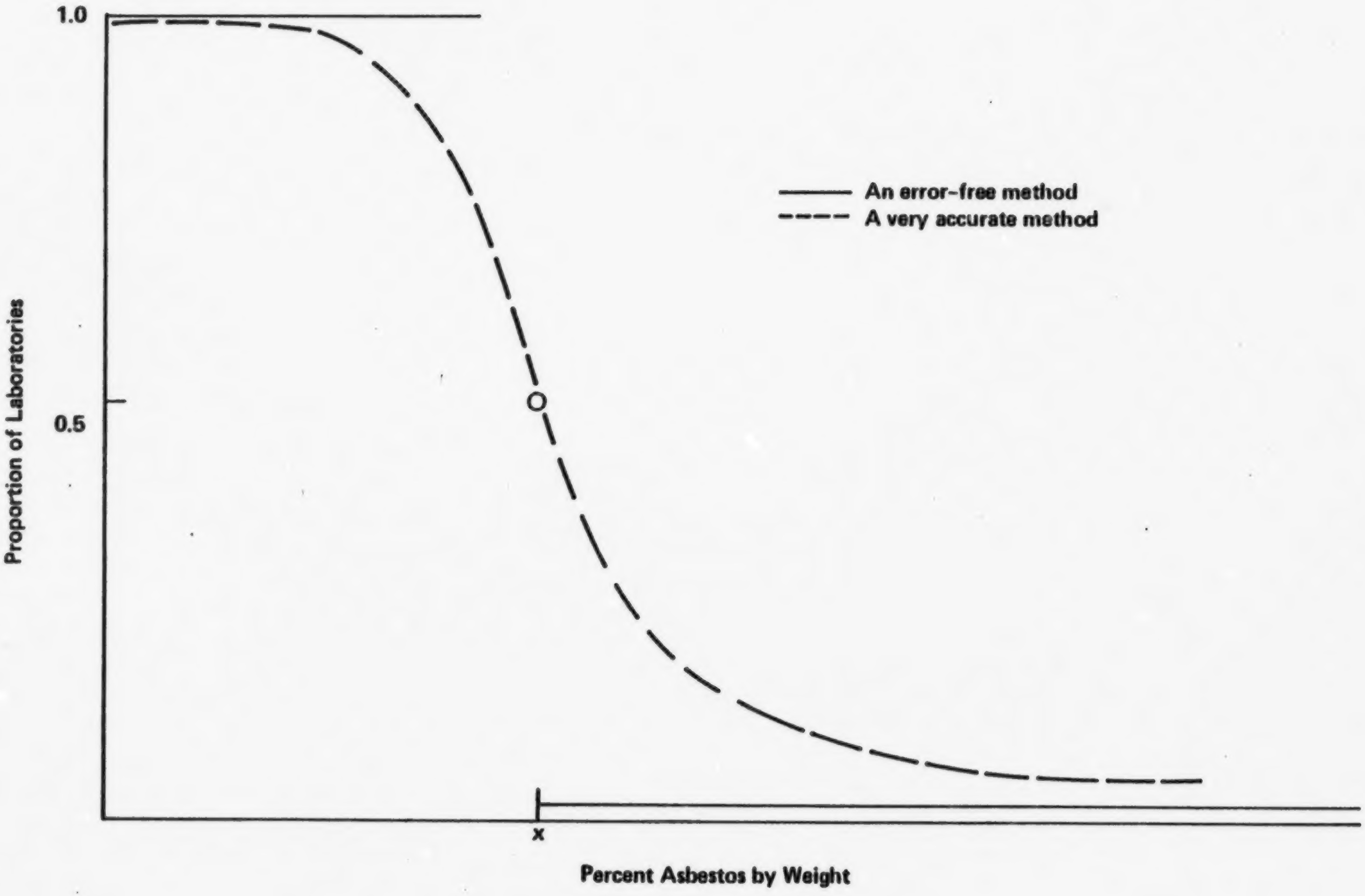


Figure 10. Theoretical operating characteristic curves.

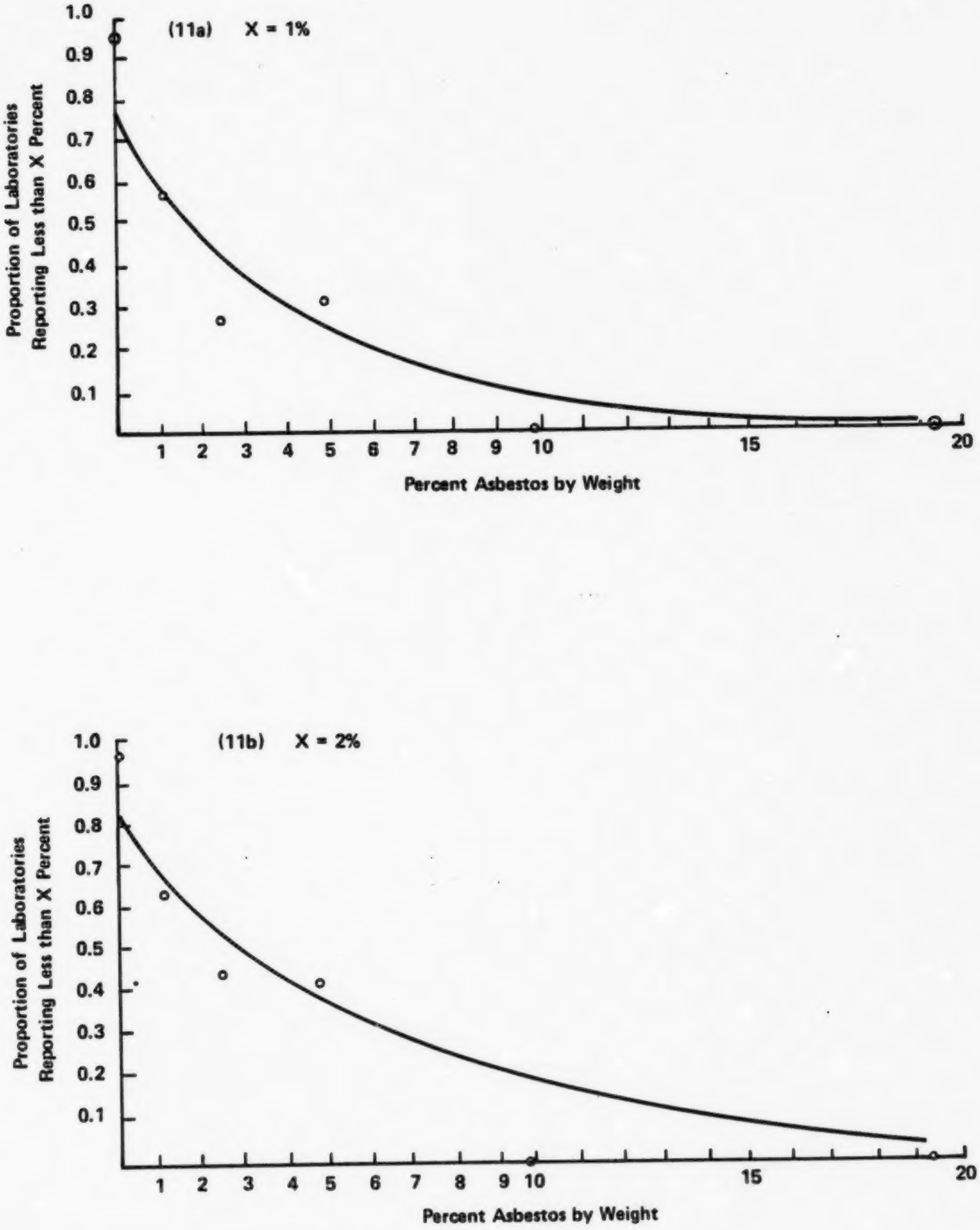
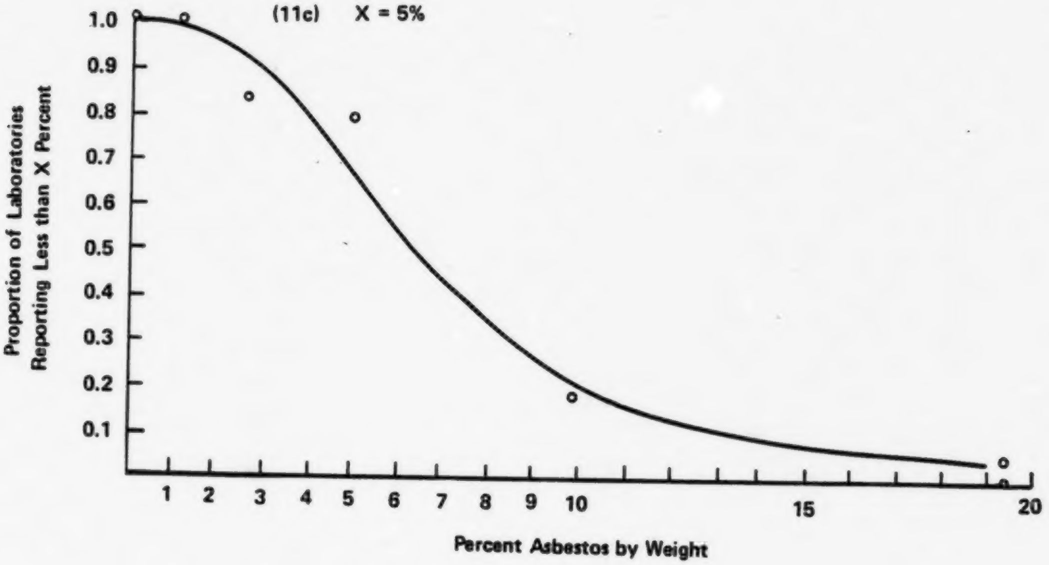


Figure 11. Operating characteristic curves for Group P data.



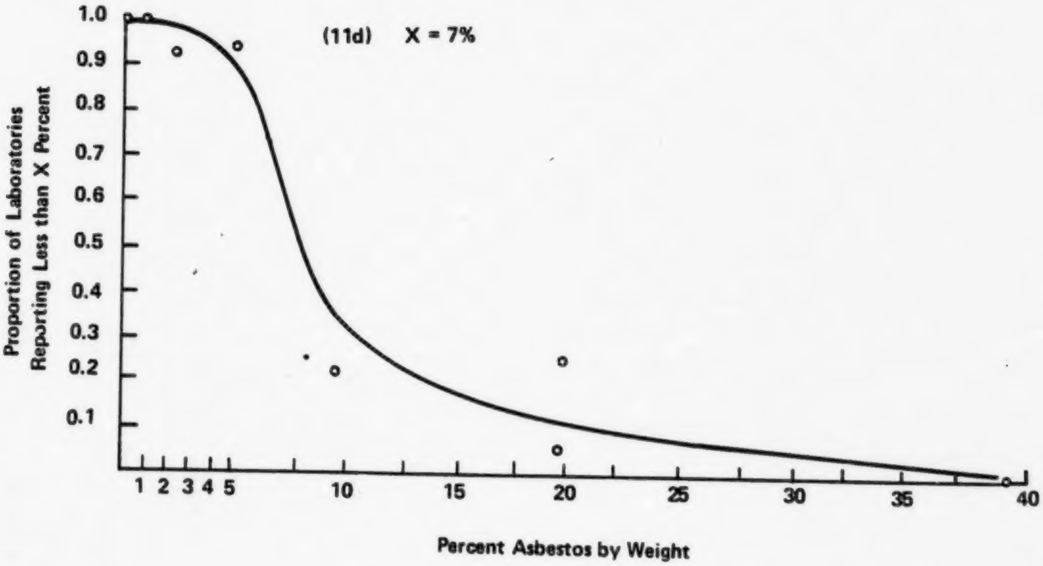


Figure 11 (continued)

This result applies only to data that have been adjusted for variance due to both laboratory differences and to asbestos type. This adjustment formally applies only to the samples and laboratories in this study and would be questionable for other laboratories and other samples of different composition. Data corrected only for variance due to asbestos type do not show the improved performance demonstrated for fully calibrated data in Figures 11c and 11d.

6.7 GENERAL OBSERVATIONS

Several general points should be made before concluding this section. Table 3 shows that between-laboratory variance on sample series J (Group P, SP(J) = 16.1) is comparable to that of similar weight percent series (SP(B) = 19.5, SP(I) = 19.6). This suggests that the formulated samples were not significantly less variable in composition than the "real-world" samples distributed and thus that the results of this study, at least with respect to precision, are reasonable estimates of what would be seen in point counting analyses of samples normally submitted to laboratories.

Several laboratories reported results by the point count method that were notably more accurate than the Group P average. Laboratories PP2, PS, PT, PV, and PW2 (Table 2) are among the more experienced of the participating laboratories in bulk sample analysis. Laboratory PP2, which reported the results most consistently close to the true weight percent values, is known to have an internal quality control program involving preparation and analysis of asbestos-containing standard samples.

It was noted earlier that some relationship may exist between Group P (point count) and Group B (both) data contributed by any one laboratory. The estimate produced by point counting may have influenced the result of the laboratory's own method, or vice versa. The problem of interpreting Group B is further complicated by comparison with Group O (other). Group O consists of data produced by laboratories that used only their own quantitation procedure. As in Groups P and B, there are differences between laboratories. Lab 04, which reported the "best" results of Group O, is one of the more experienced PLM laboratories participating in the study. However, as was shown in Section 6.1, Group O is significantly more biased than Group B. The dissimilarity of Groups B and O suggests that, although both sets of data were produced by the respective laboratories' own quantitation procedures, there is some systematic difference between the procedures used.

6.8 CONCLUSIONS

For the sake of clarity, the definitions of the groups into which the PLM data were classified are restated below.

Group P--(Point count) PLM asbestos area percent determinations by the point count method.

Group B--(Both) PLM asbestos area percent determinations by the laboratories' own methods for laboratories that also provided data by the point count method.

Group O--(Other) PLM asbestos area percent determinations by the laboratories' own methods for laboratories declining to use the point count method.

The following conclusions are indicated by the analysis of PLM data.

- A considerable amount of the variation in the data can be removed by linearly regressing the natural logarithms of area percent (reported data) on the natural logarithms of weight percent (known values). This finding is consistent with the assumption that area and weight are related by a power function.

- There is significant variation in the area/weight relationship because of differences between laboratories, differences between asbestos types (amosite and chrysotile), and interactions between laboratory and asbestos type.

- Groups P and B appear similarly biased. Group O results have a significantly higher bias than Groups P and B.

- Group P average bias (b) varies with the type and weight percent (W) of asbestos in a sample. For samples containing chrysotile, $b = 18.5$ percent at $W = 10$ and $b = -24.2$ percent at $W = 50$. For samples containing amosite, $b = 118.5$ percent at $W = 10$ and $b = 12.1$ percent at $W = 50$.

- Groups P, B, and O are similarly precise when the effects of bias are removed.

- Precision of Group P data may be described by the coefficient of variation. At a mean reported value (MP) of 10 percent asbestos, $CV \cong 79$ percent; at $MP = 20$ percent asbestos, $CV \cong 61$ percent; at $MP = 50$ percent asbestos, $CV \cong 41$ percent.

- Group P is significantly more precise than Groups B and O in terms of residual variance after removing variance due to laboratory and asbestos-type effects.

- Considerable gains in precision and accuracy of PLM data are possible by individual calibration of laboratories, especially for laboratories using point counting.

- Within-analyst variance probably accounts for less than 25 percent of the total between-laboratory variance in Group P data.

- Several false negatives and a false positive were included in point count results. The false negatives are more likely due to variability in sample and slide preparation than to the counting procedure per se. The false positive was likely due to sample contamination. The rate of false negatives is such that the analysis of three samples of a suspect material, if each contained at least 5 percent asbestos by weight, would result in three false negatives with a probability less than 0.03 and possibly as low as 0.001.

- The data, after adjustment for between-laboratory and asbestos-type effects, suggest that laboratories using the point count method are better able to resolve the difference between samples containing <7 percent and >7 percent asbestos by weight than they are able to resolve samples containing <1 percent from >1 percent.

SECTION 7

METHOD EVALUATION: X-RAY POWDER DIFFRACTION

Twelve laboratories received samples for analysis by the proposed XRD method; five laboratories participated and returned six sets of results. These data are summarized in Table 8. Three of the data sets (X1-X3) were produced by some variation of the proposed thin-layer method of quantitation; the other sets (X4-X6) were produced by alternative bulk or thick-layer methods of quantitation. The seven laboratories declining to perform the requested analyses indicated either that the method was too time-consuming and costly, they lacked adequate facilities and expertise, or they felt the method was inadequate. It should be emphasized that none of the "thin-layer" laboratories followed the Tentative Method protocol exactly; similarly, bulk methods employed by laboratories reporting X4-X6 were not strictly equivalent. A notable deviation of the actual methods employed from the Tentative Method was the failure of all laboratories to use step-scanning analysis for quantitation.

Laboratories were instructed to determine and report XRD results independently of any information derived from PLM analysis. This is not the appropriate procedure for typical laboratory analysis of submitted samples. As has been noted earlier, XRD affords information only on crystal lattice structure and not on particle morphology. The presence of asbestiform particles must be determined by an optical procedure such as PLM.

Means and standard deviations of all reported XRD results are shown in Table 9. Average reported values for XRD are shown for bulk methods, thin-layer methods, and all methods together. Except for Series G, the means of the bulk methods are closer to the reference values than those of the thin-layer methods.

Average absolute errors of reported results for bulk and thin-layer methods are shown in Table 10. Comparing the average errors with a two-

TABLE 8. REPORTED XRD RESULTS
(percent asbestos)

			Thin-layer			Bulk		
Series	Type	Weight %	X1	X2	X3	X4	X5	X6
C	Chrysotile	1.2	1.0	3.0	5.0	0.0	0.0	3.0
A	Chrysotile	4.9	3.0	7.0	0.0	3.0	9.0	1.0
E	Chrysotile	19.4	4.0	0.0	7.0	13.0	31.0	10.0
I	Chrysotile	74.5	.	55.0	45.0	.	74.0	75.0
H	Amosite	2.5	.	2.0	3.0	.	4.0	2.0
G	Amosite	9.8	.	3.0	11.0	17.0	23.0	25.0
D	Amosite	19.4	.	18.0	37.0	20.0	32.0	20.0
B	Amosite	38.5	.	53.0	69.0	51.0	75.0	30.0
F	Amosite	0	.	.	0.7	.	0.0	0.0
J	Chrysotile	~50%[a]	.	63	35	.	51	40
K	Chrysotile	(Duplicate of C,A,E, or I)	.	42(I)	15.0(E)	.	35.0(E)	1.0(C)

[a] Area percent asbestos, mean of Groups P and B.

TABLE 9. MEANS AND STANDARD DEVIATIONS OF REPORTED XRD RESULTS
(percent asbestos)

			Thin-layer		Bulk		Pooled	
Series	Type	Weight %	M	S	M	S	M	S
C	Chrysotile	1.2	3.0	2.0	1.0	1.7	2.5	1.8
A	Chrysotile	4.9	3.3	3.5	4.3	4.2	4.3	3.3
E	Chrysotile	19.4	3.7	3.5	18.0	11.4	10.8	10.9
I	Chrysotile	74.5	50.0	7.1	74.5	0.7	62.2	14.7
H	Amosite	2.5	1.5	0.7	3.0	1.4	2.8	1.0
G	Amosite	9.8	7.0	5.7	21.7	4.2	15.8	9.0
D	Amosite	19.4	28.0	12.7	24.0	6.9	25.6	8.3
B	Amosite	38.8	61.0	11.3	52.0	22.5	55.6	17.6
F	None	0	0.2	0	0	0	0	0

TABLE 10. AVERAGE ABSOLUTE ERRORS OF REPORTED XRD RESULTS
(percent asbestos)

			Average absolute error	
Series	Type	Weight %	Thin-layer (n)	Bulk (n)
C	Chrysotile	1.2	1.9 (3)	1.4 (3)
A	Chrysotile	4.9	3.0 (3)	3.3 (3)
E	Chrysotile	19.4	15.7 (3)	9.1 (3)
I	Chrysotile	74.5	24.5 (2)	0.5 (2)
H	Amosite	2.5	0.5 (2)	1.0 (2)
G	Amosite	9.8	4.0 (2)	11.9 (3)
D	Amosite	19.4	9.0 (2)	4.6 (3)
B	Amosite	38.8	22.2 (2)	18.7 (3)
F	None	0	0.7 (1)	0 (2)

n = Number of reported results.

sided t-test, there is no significant difference at the 5-percent level between laboratories performing the analyses by bulk methods and those using thin-layer methods, although, as noted above, there is a suggestion that the bulk methods are more accurate.

Estimates of precision, given by the coefficient of variation (CV), calculated as the standard deviation divided by the mean reported value, are shown in Table 11. Comparing CVs with either a sign test or a paired t-test again showed no significant difference between bulk and thin-layer methods (two-sided $P > 0.4$). Considering individual CVs, those for bulk methods are all less than or equal to those for thin-layer methods, except for Series C and B, further suggesting that the bulk methods are at least as precise as the thin-layer methods, as applied by laboratories in this study.

The overall impression from these results, that bulk analysis is at least as accurate and precise as thin-layer analysis, is further supported by the results of a more detailed analysis of both bulk and thin-layer methods by asbestos type.

Linear regression analyses of the reported results for chrysotile samples and amosite samples for bulk methods gave the following results (see Figure 12):

1. Reported results and reference values are better correlated for chrysotile than amosite (i.e., correlation coefficients are significantly different at the 5 percent level, by a two-sided t-test);

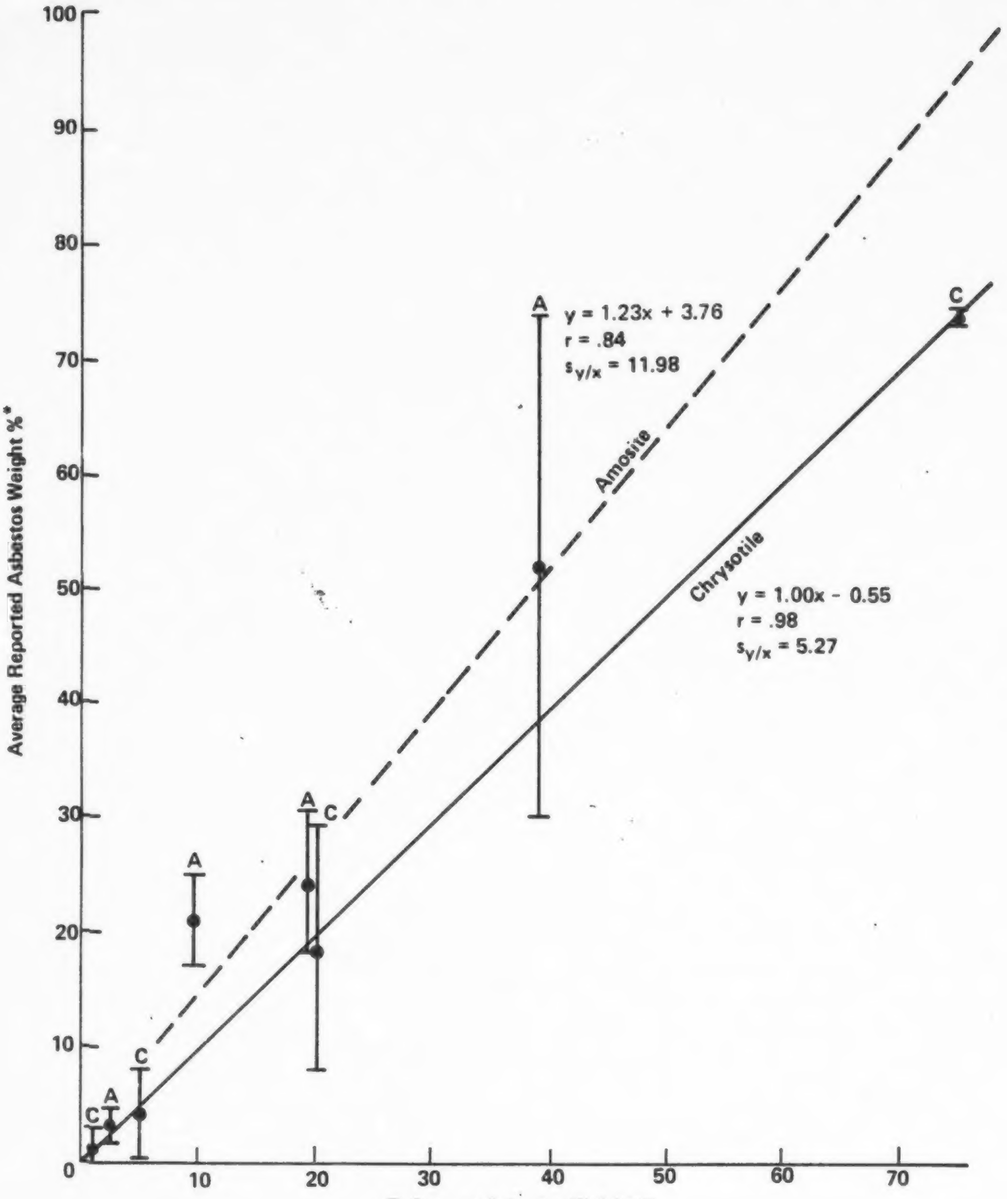
2. Analysis of chrysotile is significantly more precise than amosite (i.e., variances about the regression are significantly different at the 5 percent level by a two-sided F-test); and

3. Analysis of chrysotile appears more accurate (chrysotile slope = 1.00, intercept = -0.55; amosite slope = 1.23, intercept = 3.76), although a two-sided t-test for difference between the slopes is not significant at the 5 percent level. This is probably due to the large imprecision in the estimate of the amosite slope. The results for chrysotile in this regard are particularly striking, with the regression line being essentially indistinguishable from the theoretical $y = x$ line with slope = 1.

In contrast, linear regression analyses of the reported results by individual asbestos types for thin-layer methods (Figure 13) revealed no

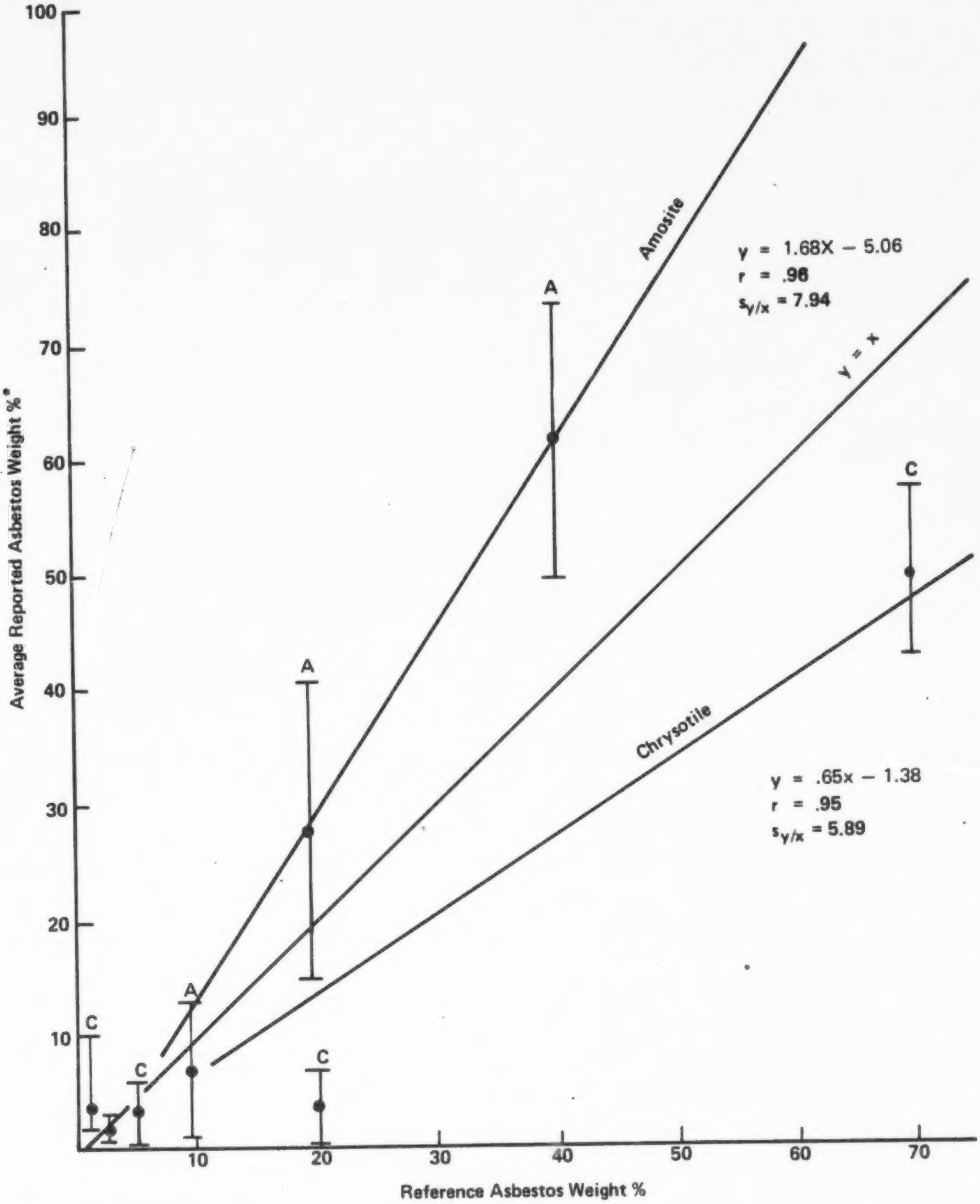
TABLE 11. COEFFICIENTS OF VARIATION OF REPORTED XRD RESULTS

Series	Type	Weight %	Coefficient of variation		
			Thin-layer	Bulk	Pooled
C	Chrysotile	1.2	0.67	1.7	0.72
A	Chrysotile	4.9	1.06	0.98	0.77
E	Chrysotile	19.4	0.95	0.63	1.0
I	Chrysotile	74.5	0.14	0.01	0.24
H	Amosite	2.5	0.47	0.47	0.36
G	Amosite	9.8	0.81	0.19	0.57
D	Amosite	19.4	0.45	0.30	0.32
B	Amosite	38.8	0.19	0.43	0.32



*Error bars represent ±1 σ.

Figure 12. Comparison of bulk XRD analysis by asbestos type.



*Error bars represent ±1 σ.

Figure 13. Comparison of thin-layer XRD analysis by asbestos type.

significant differences in correlation or precision between analyses for chrysotile and amosite; correlation coefficients and standard errors about the regression for the two asbestos types were not significantly different at the 5-percent level by a two-sided t-test. The slopes for chrysotile and amosite were, however, significantly different at the 5-percent level. Analysis for both asbestos types is biased (chrysotile, negative; amosite, positive) with slopes of the regression lines significantly different from 1.

A further comparison between bulk and thin-layer methods, by asbestos type, indicates that for analysis of chrysotile, the bulk methods are significantly less biased than thin-layer methods. A two-sided t-test indicates that the slope of 0.65 for chrysotile analysis by thin-layer methods is significantly less than that of 1.00 for chrysotile by bulk methods at the 5 percent level. No significant difference in slopes (bias) was observed between methods for amosite.

Data produced by thin-layer methods of analysis included one false negative out of three analyses of the 4.9 percent chrysotile sample. The same laboratory reported chrysotile false positives for all amosite samples and for the blank sample with reported chrysotile values ranging from <1 to 8 percent. One false negative out of three analyses was also reported at the 19.4 percent chrysotile level.

Data produced by bulk methods of analysis included two false negatives out of three analyses of the 1.2 percent chrysotile sample. One of these laboratories also reported a false positive amosite for the 4.9 percent chrysotile sample.

Four laboratories reported results on duplicate samples (Series K) included in the samples sent to the laboratories. However, because of the small number of observations, no firm conclusions can be drawn about the intralaboratory variance of this method or its relative contribution to the total variance of the reported results.

These results do give evidence that XRD is capable of detecting chrysotile at the 1 percent level in a simple matrix and suggest that at this level a thin-layer method of analysis may be more reliable. Further investigation is required to determine reliable detection limits over a variety of sample materials for both bulk and thin-layer methods. Although it is problematic whether such limits could be firmly established given the matrix dependency of the sensitivity of the method and the extreme variability observed in bulk insulation matrix materials, sensitivity would be expected to improve if step-scanning analysis were routinely employed.

It should be emphasized that because of the small number of laboratories participating in this study and the diversity of methods actually employed, it is not possible to draw any firm conclusions from the results of these analyses. However, the following observations can be made:

1. The bulk methods appear to be at least as accurate and precise as thin-layer methods over the range of samples included in this study and significantly more accurate for the analysis of chrysotile; and
2. There is a suggestion that thin-layer methods of analysis may be more reliable (i.e., more sensitive) than bulk methods at the 1 percent level of chrysotile in a simple matrix.

Since chrysotile is the most commonly occurring asbestos mineral in bulk insulation materials, and since most laboratories routinely performing quantitative analysis of asbestos in insulation samples use a bulk method of analysis, the first observation suggests that for a wide-scale screening program, use of bulk methods of XRD analysis, ancillary to PLM, should be given further consideration. It should be noted, however, that the suggestion that bulk methods are at least as accurate and precise as thin-layer methods may be due to the fact that the laboratories performing the analyses by bulk methods were more experienced in this method of analysis than those using thin-layer methods. The second observation indicates a need to further evaluate both methods at the 1 percent level of detection. Recommendations for further development and evaluation of both bulk and thin-layer methods are detailed in Section 3.2.

SECTION 8

COMMENTS

Comments made by participating laboratories in written reports were a valuable source of information for this technical evaluation and may contribute to future methods refinement. Selected comments under consideration are discussed below.

Commenting on PLM, analysts most frequently voiced concern over the additional time and effort required for quantitative analysis by point counting. Estimates of the impact of the PLM quantitative section cite doubled and tripled analysis times and projected cost increases of 150 to 200 percent. Analysts objected most strongly to the use of point counting on samples containing a relatively high percentage of asbestos, e.g., more than 30 percent. It is felt that the objectivity of the quantitative estimation procedure is not as critical at this level as it is in the 1 to 10 percent range. Additionally, eye fatigue reduces the number of samples an analyst can analyze per day by point counting. Practice and greater familiarity with the method may, however, bring analysis time more in line with that of current procedures. The use of a staged counting process that would allow the counting of fewer points on high percentage samples could be investigated.

There were some problems with application of the PLM method. Specifically, some operators were biased toward picking out fibers and found it difficult to subsample "randomly." Also, teasing the sample apart with forceps and/or dissecting needles resulted in an uneven distribution of sample material on the microscope slide. This is in contrast to the experience of one laboratory that milled all samples before analysis. Milling samples results in a finer grained material that can be distributed more evenly on slides. However, milling may disrupt fiber bundles or comminute fibers to <3 μm in length, thus distorting the results of quantitative analysis or making fibers more difficult to identify.

Overlaying particles (i.e., asbestos fibers superimposed on matrix, or vice versa) were also a problem in the analysis for which no guidance was offered. The method has been modified to require that a point be scored for both categories when overlays occur.

Several reports commented that the definition of "fiber" used in the method was confusing and did not require positive identification of the particles as asbestos. Changes in the text have been made to correct this discrepancy.

Two errors in the computation of the confidence interval (CI) were discovered and corrected. On page 10 of the protocol, the CI should be ±0.035 instead of 0.018. On the PLM reporting form (Appendix D), the square root symbol was omitted. Most laboratories realized this error and corrected for it in their reports. It is recommended elswhere in this report that the CI computation be deleted from the method.

Analysts at one laboratory provided extensive review comments on the PLM protocol. The reviewers felt primarily that reliable quantitative analysis is not possible using microscopical techniques without allied quantitative chemical and physical procedures, which should be separate from and more stringently specified than sample preparation procedures for qualitative PLM analysis. The following points were emphasized in support of their recommendation.

1. Subsamples of a bulk material taken with forceps are unlikely to be representative;
2. The method does not contain a description of how subsamples are to be uniformly dispersed on the microscope slide;
3. Grinding a sample with mortar and pestle, an optional sample preparation step, may cause separation of amphibole bundles, which would bias point counting results;
4. Grinding a sample with a Wylie mill, an optional sample preparation step, may cause the shearing of particles with fibrous habit (>3:1 aspect ratio) from prismatic particles;
5. Step-by-step descriptions should be given of quantitative matrix reduction procedures (specifically, low-temperature ashing, NaOH and CH_3COOH dissolution, and gravimetric calculations) with instructions as to when they are to be used on representative sample types most frequently encountered.

An additional objection raised was that point counting does not provide for the quantitation of phases that occur as coatings, such as binders and resins.

It is recognized that all sample preparation steps prior to point counting must be performed quantitatively for analytical results to be meaningful. However, absolute standardization of such procedures has not been thought feasible for bulk samples because of the extreme range of sample composition encountered. Several other reviewers with considerable analytical experience have stated that for the majority of samples no matrix reduction should be performed. Sample preparation procedures were therefore included in the method as optional steps to be used at the discretion of the analyst. Further systematic investigation would be required to determine if stricter guidelines could be successfully applied.

The quantitative XRD procedure in the Tentative Method is more time consuming and costly than alternative bulk techniques. Results of the study further indicate that at this time very few laboratories are set up to perform the thin-layer analysis as prescribed. Several comments were received concerning obstacles to the generalized use of quantitative XRD methodology.

Acquisition of appropriate asbestos standards is expected to be a major problem. UICC standards are not exceptionally pure and are reported to be in increasingly short supply. It is essential that reliable sources of standard materials be identified and that the purity of the standards be known or determined before accurate calibration curves can be obtained.

The problem of obtaining comparability between standard and sample asbestos materials is of critical importance, with no easy or straightforward solution immediately presenting itself.

The main drawback to the thin-layer procedure as applied to bulk samples is the sample preparation step. The requirement to grind the sample to pass a 10-μm sieve is not only time consuming and costly but may not be feasible for all samples. Furthermore, because the matrix material itself may alter the asbestos grinding characteristics, the validity of standards prepared in a manner similar to sample materials is questionable.

Two typographical errors were detected in the XRD protocol and have been corrected. Specifically, in Section 7.2.3.9 (line 6), "0.1 mg," the total sample weight deposited on the silver membrane filter for analysis, should read "ca. 1 mg." In Table 2 (line 4), the powder diffraction file number for nonfibrous "amosite" should read 17-745 instead of 17-795. Participating laboratories have been notified of both changes to the protocol.

SECTION 9

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APPENDIX A

STATISTICAL PROCEDURES

APPENDIX A

STATISTICAL PROCEDURES

A.1

$$\text{Mean squared error (MSE)} = \frac{1}{n} \sum_{i=1}^{n} (w_i - w)^2$$

$$\text{Sample variance } (S^2) = \frac{1}{n} \sum_{i=1}^{n} (w_i - \bar{w})^2$$

where w = true value,

$\bar{w} = \frac{1}{n} \sum_{i-1}^{n} w_i$ is the average of the w_i, and

$i = 1, 2, \ldots n$.

If Bias = Average Error = $\bar{w} - w$;

$$\text{MSE} = \frac{1}{n} \sum_{i=1}^{n} (w_i - w)^2$$

$$= \frac{1}{n} \sum_{i=1}^{n} (w_i - \bar{w} + \bar{w} - w)^2$$

$$= \frac{1}{} \sum_{i=1}^{n} (w - \bar{w})^2 + 2(\bar{w} - w) \frac{1}{} \sum_{i=1}^{n} (w - \bar{w}) + \frac{1}{} \sum_{i=1}^{n} (\bar{w} - w)^2$$

$$= \frac{1}{n} \sum_{i=1}^{n} (w_i - \bar{w})^2 + n(\bar{w} - w)^2$$

$\therefore$ MSE = Variance + Bias^2 .

A.2

The importance of accounting for asbestos and laboratory effects can be seen from the results in Table A-1. The variable LA was regressed on LW,

TABLE A-1. LABORATORY AND ASBESTOS TYPE EFFECTS REGRESSION

```
                          GENERAL LINEAR MODELS PROCEDURE

DEPENDENT VARIABLE: LA

SOURCE                  DF      SUM OF SQUARES          MEAN SQUARE        F VALUE

MODEL                   52      1264.90720382          24.32513854         197.97

ERROR                   76         9.33829846           0.12287235         PR > F

UNCORRECTED TOTAL      128      1274.24550228                               0.0001

R-SQUARE              C.V.            STD DEV              LA MEAN

0.992672           11.8207         0.35053152           2.96539418

SOURCE                  DF         TYPE I SS    F VALUE     PR > F

ASB                      2     1139.72447794    4637.84     0.0001
LAB                     16       27.10027764      13.78     0.0001
LW                       1       83.04540990     675.87     0.0001
LW*ASB                   1        0.71692807       5.83     0.0181
LW*LAB                  16        5.80641014       2.95     0.0008
ASB*LAB                 16        8.51370013       4.33     0.0001

SOURCE                  DF        TYPE IV SS    F VALUE     PR > F

ASB                      1        5.50190254      44.78     0.0001
LAB                     16       18.04698663       9.18     0.0001
LW                       1       21.66884286     176.35     0.0001
LW*ASB                   1        0.90092383       7.33     0.0084
LW*LAB                  16        5.87623781       2.99     0.0007
ASB*LAB                 16        8.51370013       4.33     0.0001
```

with both slope and intercept allowed to vary with asbestos type and laboratory. The third order interaction term LW*ASB*LAB was not significant ($P>.5$) and the regression was rerun without this term. All the remaining terms are highly significant.

A.3

To test for differences in bias between Groups P, B, and O, weighted GLM regressions were performed in logarithmic coordinates allowing slopes and intercepts to vary with group and with asbestos type. The weights for these regressions were obtained from preliminary regressions of standard deviations on means of logarithms of reported results. The relations did not change significantly with Group (P, B, O), so the same line was used for all three groups. The results of the full regression are shown in Table A-2. Allowing all effects and interactions among GROUP, ASB and LW, three of the interaction terms were insignificant ($P > 0.5$). The regression was rerun with these interactions omitted. Results are in Table A-3, and show Groups P and B to be similarly biased ($P = 0.34$, not significant) while Group O is more biased than Group P ($P \ll 0.01$).

A.4

The regression related the logarithm of group standard deviations (LS) to the logarithm of group means (LM) using the model

$$\log s = a \log \bar{x}(1 - \bar{x}) + b + \text{error} .$$

The function $\bar{x}(1 - \bar{x})$ was employed because it produced a higher overall correlation ($R^2 = 0.98$) than the regression using $\bar{x}$ ($R^2 = 0.93$). The regression parameters a and b did not vary significantly with asbestos type for any of the groups (P, B, O). By this analysis, Groups P, B, and O are not significantly different with respect to precision ($P > 0.3$ for all pairwise comparisons of slopes and intercepts).

A.5

The following steps were used in transforming reported area percent data to predicted weights ($A \rightarrow \hat{W}$). All regressions were performed in two ways: (1) unweighted; and (2) weighted for differences in variance between sample series. No discrepancies between weighted and unweighted regressions

TABLE A-2. GROUP EFFECTS REGRESSION, ALL INTERACTIONS

```
                              GENERAL LINEAR MODELS PROCEDURE

DEPENDENT VARIABLE: LA
WEIGHT:             VINV

SOURCE                  DF        SUM OF SQUARES          MEAN SQUARE        F VALUE

MODEL                   12        11992.90965729         999.40913811         795.70

ERROR                  215          270.04237854           1.25601106        PR > F

UNCORRECTED TOTAL      227        12262.95203583                              0.0001

R-SQUARE              C.V.               STD DEV              LA MEAN

0.977979           37.4318            1.12071899           2.99402753

SOURCE                  DF           TYPE I SS    F VALUE    PR > F

ASB                      2      11465.97908739    4564.44    0.0001
GROUP                    2         21.77609024       8.67    0.0002
LW                       1        491.88689282     391.63    0.0001
ASB*GROUP                2          2.48258002       0.99    0.3739
LW*ASB                   1          9.26815889       7.38    0.0071
LW*GROUP                 2          1.31450236       0.52    0.5933
LW*ASB*GROUP             2          0.20234557       0.08    0.9226

SOURCE                  DF         TYPE IV SS    F VALUE    PR > F

ASB                      1         18.52376106      14.75    0.0002
GROUP                    2          5.98280410       2.38    0.0948
LW                       1        251.57698105     200.30    0.0001
ASB*GROUP                2          0.68701153       0.27    0.7610
LW*ASB                   1          7.96477971       6.34    0.0125
LW*GROUP                 2          1.25448030       0.50    0.6076
LW*ASB*GROUP             2          0.20234557       0.08    0.9226
```

TABLE A-3. GROUP EFFECTS REGRESSION, SIGNIFICANT INTERACTIONS

```
                          GENERAL LINEAR MODELS PROCEDURE

DEPENDENT VARIABLE: LA
WEIGHT:             VINV
                                                                                   F VALUE
SOURCE                   DF      SUM OF SQUARES            MEAN SQUARE
                                                                                   1611.52
MODEL                     6      11988.93065277          1998.15510879
                                                                                   PR > F
ERROR                   221        274.02138306             1.23991576
                                                                                    0.0001
UNCORRECTED TOTAL       227      12262.95203583

                                                               LA MEAN
R-SQUARE                C.V.            STD DEV
                                                            2.99402753
0.977655             37.1912         1.11351505

SOURCE                   DF           TYPE I SS     F VALUE     PR > F

ASB                       2      11465.97908739     4623.69     0.0001
GROUP                     2         21.77609024        8.78     0.0002
LW                        1        491.88689282      396.71     0.0001
LW*ASB                    1          9.28858232        7.49     0.0067

SOURCE                   DF          TYPE IV SS     F VALUE     PR > F

ASB                       1         22.70578530       18.31     0.0001
GROUP                     2         21.46203795        8.66     0.0002
LW                        1        363.32102770      293.02     0.0001
LW*ASB                    1          9.28858232        7.49     0.0067

                                                 T FOR H0:       PR > |T|      STD ERROR OF
PARAMETER                     ESTIMATE       PARAMETER=0                          ESTIMATE

ASB       AMOSI           1.84693236 B              9.47         0.0001        0.19494697
          CHRYS           0.79683223 B              5.16         0.0001        0.15450008
+GROUP    B               0.08772182 B              0.95         0.3447        0.09263928
          O               0.41351216 B              4.16         0.0001        0.09939073
          P               0.00000000 B               .            .             .
LW                        0.74951994 B             18.18         0.0001        0.04122674
LW*ASB    AMOSI          -0.20664948 B             -2.74         0.0067        0.07550152
          CHRYS           0.00000000 B               .            .             .
```

+Bias comparison, B and O vs. P.

were found with respect to the significance of various effects. Attention will be focused only on the results of unweighted regressions.

For each group (P, B, O), the following sequence of regressions was performed.

1. Regress LW (log of nominal weight percent) on LA (log of reported result) for each combination of laboratory and asbestos type. That is, estimate the slopes and intercepts of $LW = c(asb,lab) \cdot LA + d(asb,lab)$. The functional notation stresses the dependence of slopes and intercepts on asbestos type and laboratory, as discussed in Section 5.5.

2. Using the parameters estimated in 1, adjust the reported data A to

$$W^* = e^d A^c \ .$$

3. Regress W on W*, with forced zero intercept, according to

$$W = rW^* \ .$$

4. Using the parameters estimated in 1 and 3 (c and $b = re^d$), transform W* to predicted weights W.

$$\hat{W} = bAW^{*c} \ .$$

The predicted weight $\hat{W}$ corresponding to each reported result is thereby obtained.

The reason for step 3 is that the regressions in Step 1 tend to balance out errors in sign and magnitude. However, if equal errors, opposite in sign, are exponentiated, then an imbalance occurs. The regression in 3 is designed to compensate for this, and can be achieved with a hand calculator by entering every (W*, W) pair a second time as (-W*, -W).

APPENDIX B

TENTATIVE METHOD

March 1980

Revisions have been made to the Tentative Method pursuant to the conclusions of this study. Appendix B should not be used by laboratories as a reference or analytical protocol. Current editions of the Interim Method for the Determination of Asbestos in Bulk Insulation Samples are available from Gene Brantly, Research Triangle Institute, 800-334-8571.

TENTATIVE METHOD FOR THE DETERMINATION OF ASBESTIFORM MINERALS IN BULK INSULATION SAMPLES BY POLARIZED LIGHT MICROSCOPY AND X-RAY POWDER DIFFRACTION

A tentative method is carefully drafted from available source information. This method is still under investigation and therefore is subject to revision.

Environmental Monitoring Systems Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

March 1980

B-2

POLARIZED LIGHT MICROSCOPY

1. Principle and Application

1.1 Bulk samples of building materials taken for asbestos identification are first examined for homogeneity and preliminary fiber identification at low magnification. When discrete layers are identified, each is treated as a separate material and should receive individual characterization. Positive identification of suspect fibers is made by analysis of subsamples with the polarized light microscope. Asbestos quantitation is performed by a point-counting procedure.

1.2 This method is applicable to all bulk samples submitted for identification and quantitation of asbestos components.

2. Range

The range of the analysis is dependent on the amount of material examined. Quantities of asbestos in a building material sample will be subject to wide variation in reported results because of sampling variation in an inhomogeneous matrix. Quantities below 1 percent are reported as "<1%". The upper detection limit is 100 percent. There is no measure of sensitivity presently available.

3. Interferences

Fibrous organic and inorganic constituents may pose a challenge to identification, separation, and quantitation of the asbestiform mineral content. Spray-on binder materials may coat fibers to impart color and obscure optically determined parameters to the extent of masking the fiber identity. Fine particles of other materials may also adhere to fibers to an extent sufficient to cause confusion in identification.

4. Precision and Accuracy

Adequate data for accuracy and precision measurements are not currently available.

5. Apparatus

5.1. Analysis

5.1.1. A low-power binocular microscope, preferably stereoscopic, is used to examine the bulk insulation sample as received.

5.1.1.1. Microscope: binocular, 10-45X.

5.1.1.2. Light Source: incandescent or fluorescent.

5.1.1.3. Forceps, Dissecting Needles, and Probes

5.1.1.4. Glassine Paper or Clean Glass Plate

5.1.2. Sample preparation apparatus requirements will depend upon the insulation sample type under consideration. Various physical and/or chemical means must be employed for an adequate sample assessment.

5.1.2.1. Ventilated Hood or negative pressure glove box.

5.1.2.2. Microscope Slides

5.1.2.3. Coverslips

5.1.2.4. Disposable gloves.

5.1.2.5. Mortar and Pestle: agate or porcelain. (optional)

5.1.2.6. Wylie Mill (optional)

5.1.2.7. High-Speed Blender (optional)

5.1.2.8. 100-mL Beakers and Assorted Glassware (optional)

5.1.2.9. Centrifuge (optional)

5.1.3. Compound microscope requirements: A polarized light microscope complete with polarizer, analyzer, port for wave retardation plate, 360° graduated rotating stage, substage condenser, lamp, and lamp iris.

5.1.3.1. Polarized Light Microscope: described above.

5.1.3.2. Objective Lenses: 10X, 25X, and 45X or near equivalent.

5.1.3.3. Dispersion Staining Objective Lens (optional)

5.1.3.4. Ocular Lens: 10X minimum.

5.1.3.5. Eyepiece Reticle: cross hair or 25 point (Available from Preiser Scientific and other microscope distributors)

5.1.3.6. Michel-Lévy Interference Color Chart

5.1.3.7. Red I Retardation Plate (First-order compensator)

5.1.3.8. Abbe Refractometer (optional)

6. Reagents

6.1. Sample Preparation

6.1.1. Distilled Water

6.1.2. 0.5 N H_2SO_4: ACS reagent grade (optional)

6.1.3. 0.5 N HCl: ACS reagent grade (optional)

6.1.4. Sodium metaphosphate $(NaPO_3)_6$ (optional)

6.2. Analytical Reagents

6.2.1. Refractive Index Liquids: 1.490-1.570, 1.590-1.720 in 0.002- or 0.004-step increments.

6.2.2. Refractive Index Liquids for Dispersion Staining: high-dispersion series, 1.550, 1.605, 1.630.

6.2.3. UICC Asbestos Reference Sample Set: Available from: UICC MRC Pneumoconiosis Unit, Llandough Hospital, Penarth, Glamorgan CF6 1XW, UK.

6.2.4. Tremolite-asbestos (source to be determined)

6.2.5. Actinolite-asbestos (source to be determined)

7. Procedures

NOTE: Exposure to airborne asbestos fibers is a health hazard. Bulk samples submitted for analysis are usually friable and may release fibers during handling or matrix reduction steps. All sample and slide preparation should be carried out in a ventilated hood or glove box with continuous airflow (negative pressure). Handling of samples without these precautions may result in exposure of the analyst and contamination of samples by airborne fibers. The level of airborne fibers should be monitored in accordance with NIOSH Analytical Method #P&CAM 239: Asbestos Fibers in Air (see DHEW/NIOSH publication no. 79-127, February 1979).

Refractive index liquids typically contain several toxic compounds, including brominated naphthalene, brominated and iodinated ring compounds, and hydrogenated terphenyls. Disposable gloves should be worn by the analyst to avoid prolonged skin contact with these materials. Prepared slides and waste bulk material should be disposed of in accordance with proper procedures for toxic substances. Asbestiform materials should be double-bagged, labelled, and buried in appropriate landfill or burial sites.

7.1 Sampling: Samples for analysis of asbestos content shall be taken in the manner prescribed in the guidance document Asbestos-Containing Materials in School Buildings, EPA #C00090, part 1. If there are any questions about the representative nature of the sample, another sample should be requested before proceeding with the analysis.

7.2 Analysis

7.2.1. Gross Examination: Bulk samples of building materials taken for the identification and quantitation of asbestos are first examined for homogeneity at low magnification with the aid of a stereomicroscope. The core sample is carefully removed from the sampling canister onto a glassine transfer paper or clean glass plate. If possible, note is made of the top and bottom orientation. When discrete strata are identified, each is treated as a separate material so that fibers are identified and quantitated in that layer only.

7.2.2. Sample Preparation: Bulk materials submitted for asbestos analysis involve a wide variety of matrix materials. Representative subsamples may not be readily obtainable by simple means in heterogeneous materials, and various steps may be required to alleviate the difficulties encountered. In most cases, however, the best preparation is made by using fine-pointed forceps to sample at several places from the bulk material. Forcep samples are immersed in a refractive index liquid on a microscope slide, teased apart, covered with a cover glass, and observed with the polarized light microscope.

Alternatively, attempts may be made to homogenize the sample or eliminate interferences before further characterization. The selection of procedure is dependent upon the samples encountered and personal preference. The following are presented as possible methods.

A mortar and pestle can sometimes be used in size reduction of soft or loosely bound materials thougn this may cause matting of some samples. Such samples may be reduced in a Wylie mill. Apparatus should be clean and extreme care exercised to avoid cross-contamination of samples. Periodic checks of the particle sizes should be made during the grinding operation so as to preserve any fiber bundles present in an identifiable form.

Treatment may occasionally be required to eliminate interferences. For cementitious materials, dissolution of the calcareous substances may be effected with warm dilute sulfuric acid (0.5 N at 65° C) [8]. Calcite may be dissolved with warm dilute hydrochloric acid [9]. Wash twice with distilled water, being careful not to lose the particulates during decanting steps. Centrifugation of the suspension will prevent significant fiber loss. Prolonged acid contact with the sample may alter the optical characteristics of chrysotile fibers and should be avoided.

Coatings and binding materials adhering to fiber surfaces may be removed by treatment with sodium metaphosphate [10]. Add 10 mL of 10 g/L sodium metaphosphate to a small (0.1 to 0.5 mL) sample of bulk material in a 15-mL glass centrifuge tube. For approximately 15 seconds each, stir the mixture on a vortex mixer, place in an ultrasonic bath and then shake by hand. Repeat the series. Boil the contents of the tube over a bunsen flame for about 20 seconds. Collect the dispersed solids by centrifugation at 1000 rpm for 5 minutes. Wash the sample three times by suspending in 10 mL distilled water and recentrifuging. After washing, resuspend the pellet in 5 mL distilled water, place a drop of the suspension on a microscope slide, and dry the slide at 110° C.

In samples with a large portion of cellulosic or other organic fibers, it may be useful to ash part of the sample and view the residue. Ashing should be performed at temperatures below 550° C. It should not be performed in an open flame or high-temperature oven because dehydration of the asbestos minerals results in changes of refractive index and other key parameters, and possible artifact formation. Ashing and acid treatment of samples should not be used as standard procedure. In order to monitor possible changes in fiber characteristics, the material should be viewed microscopically before and after any sample preparation procedure. Use of these procedures on samples to be used for quantitation requires a correction for percent weight loss.

7.2.3. Fiber Identification: Positive identification of asbestos requires the determination of the following optical properties.

Morphology
Color and pleochroism
Refractive indices
Birefringence
Extinction characteristics
Sign of elongation

Table 1 lists the above properties for commercial asbestos fibers. Figure 1 presents a flow diagram of the examination procedure. Natural variations in the conditions under which deposits of asbestiform minerals are formed will occasionally produce exceptions to the published values and differences from the UICC Standards. The sign of elongation is determined by use of the Red I retardation plate and crossed polars. Refractive indices may be determined by either the Becke line test or dispersion staining. Becke lines are maximized by viewing with a nearly closed substage diaphragm.

TABLE 1. OPTICAL PROPERTIES OF ASBESTOS FIBERS*

Mineral	Morphology, color[a]	Refractive indices[b] α	Refractive indices[b] γ	Birefringence (avg. γ-α)	Extinction angle (degrees)	Sign of elongation
Chrysotile	Wavy fibers. Fiber bundles have splayed ends and "kinks". Aspect ratio typically >10:1. Colorless[c], nonpleochroic.	1.493-1.560	1.517-1.562	.013	0	+
"Amosite"	Straight, rigid fibers. Aspect ratio typically >10:1. Brownish, nonpleochroic. Opaque inclusions may be present.	1.635-1.696	1.655-1.729	.027	0	+
Crocidolite	Straight fibers, less rigid than amosite. Thick fibers and bundles common, blue to purple-blue in color. Pleochroic. Birefringence as low as 0.004.	1.654-1.701	1.668-1.717	.015	0	-
Anthophyllite-asbestos	Straight fibers and acicular cleavage fragments.[d] Some composite fibers. Aspect ratio <10:1. Colorless to light brown.	1.596-1.652	1.615-1.676	.022	0	+
Tremolite-actinolite-asbestos	Normally present as acicular or prismatic cleavage fragments[d]. Single crystals predominate. Aspect ratio <10:1. Colorless to pale green.	1.599-1.668	1.622-1.688	.022	0-20°[e]	+

[a] From reference 1.

[b] From reference 2.

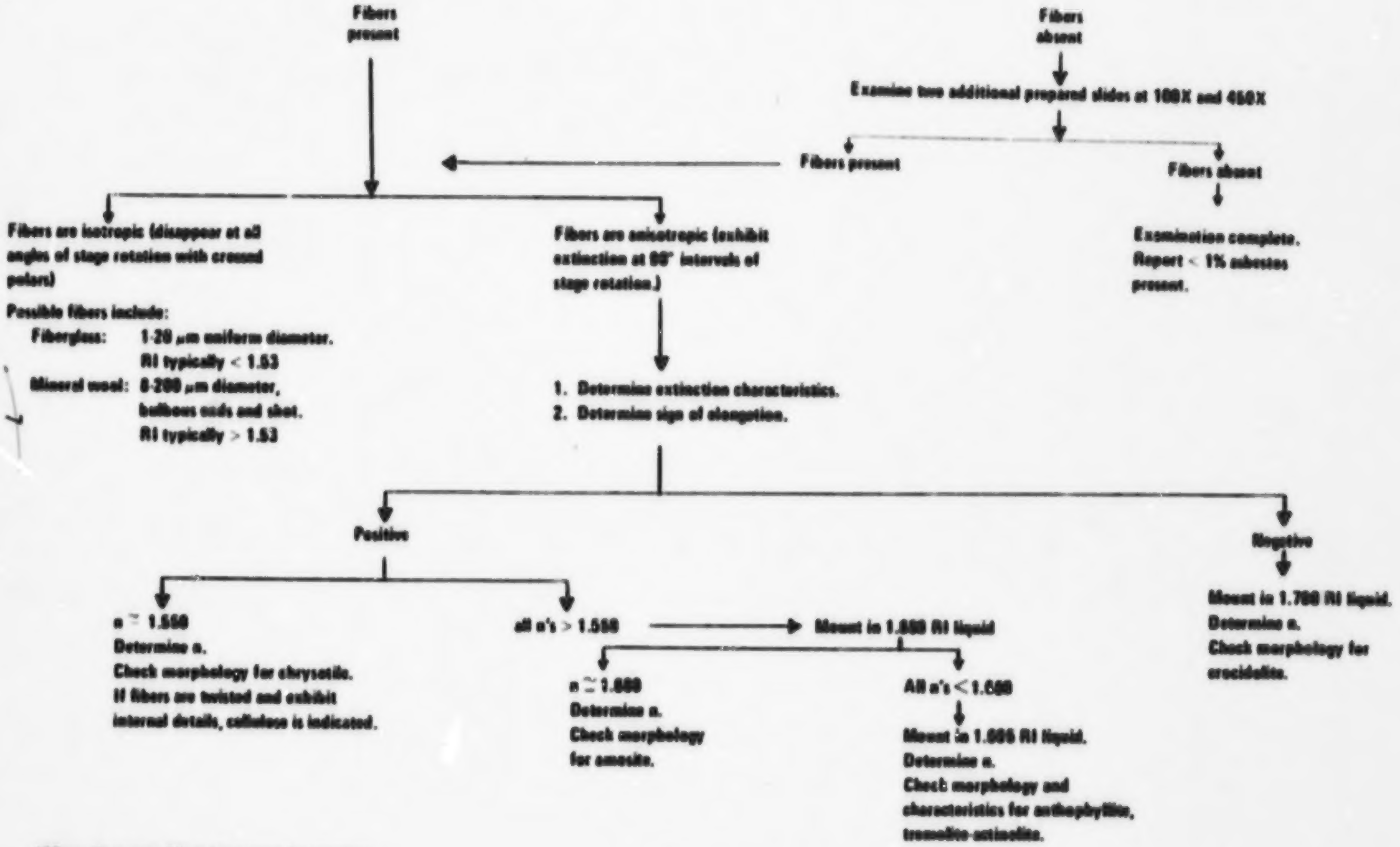
[c] Fibers subjected to heating may be brownish.

[d] Fibers defined as having aspect ratio >3:1.

[e] Extinction angle for fragments. Composite fibers extinguish at 0°.

*Some information in Table 1 has been revised for current editions of the PLM method.

Polarized light microscopy analysis: For each type of material identified by examination of sample at low magnification. Mount spacially dispersed sample in 1.550 RI liquid. (If using dispersion staining, mount in 1.550 HD.) View at 100X with both plane polarized light and crossed polars.*


Fibers present
Fibers absent
Examine two additional prepared slides at 100X and 450X
Fibers present
Fibers absent
Examination complete.
Report < 1% asbestos present.
Fibers are isotropic (disappear at all angles of stage rotation with crossed polars)
Possible fibers include:
Fiberglass: 1-20 μm uniform diameter.
RI typically < 1.53
Mineral wool: 8-200 μm diameter, bulbous ends and shot.
RI typically > 1.53
Fibers are anisotropic (exhibit extinction at 90° intervals of stage rotation.)
1. Determine extinction characteristics.
2. Determine sign of elongation.
Positive
Negative
n ≃ 1.550
Determine n.
Check morphology for chrysotile.
If fibers are twisted and exhibit internal details, cellulose is indicated.
all n's > 1.550
Mount in 1.680 RI liquid
n ≃ 1.680
Determine n.
Check morphology for amosite.
All n's < 1.680
Mount in 1.605 RI liquid.
Determine n.
Check morphology and characteristics for anthophyllite, tremolite-actinolite.
Mount in 1.700 RI liquid.
Determine n.
Check morphology for crocidolite.

7

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*More than one fiber type may be present.

Figure 1. Flow chart for analysis of bulk samples by polarized light microscopy.

Inexperienced operators may find that the dispersion staining technique is more easily learned, and should consult references 3 and 6 for guidance. Central stop dispersion staining colors are presented in Table 2. Available high-dispersion (HD) liquids should be used.

7.2.4. Quantitation of Asbestos Content: Asbestos quantitation is performed by a standard point-counting procedure. An ocular reticle is used to visually superimpose a point or points on the microscope field of view. Record the number of points positioned directly above each kind of particle or fiber of interest. Score only points directly over asbestos fibers or non-asbestos matrix material. Do not score empty points for the closest particle. This provides a determination of the areal percent asbestos. Reliable conversion of areal percent to percent of dry weight is not currently feasible unless the specific gravities and relative volumes of the materials are known.

For the purpose of this method, "fibers" are defined as having an aspect ratio greater than 3:1 and substantially parallel borders.[*]

A total of 400 points superimposed on either asbestos fibers or non-asbestos matrix material must be counted over at least eight different preparations of representative subsamples. Take eight fine-pointed forcep samples and mount each separately with the appropriate refractive index liquid. Count 50 nonempty points on each preparation, using either

1. A cross-hair reticle and mechanical point-counting stage; or
2. A reticle with 25 points and counting at least 2 randomly selected fields.

For samples with mixtures of isotropic and anisotropic materials present, viewing the sample with slightly uncrossed polars or the addition of a Red I retardation plate to the polarized light path will allow simultaneous discrimination of both fiber types. Quantitation should be performed at the lowest magnification of the polarized light microscope which can effectively distinguish the sample components. Confirmation of the quantitation result by a second analyst on some percentage of analyzed samples should be used as standard quality control procedure.

If seven or fewer of 400 non-empty points are scored for asbestos fiber, report <1 percent asbestos.[+] For all other results, the percent asbestos is calculated as follows:

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[*] and being positively identified as asbestos.

[+] omitted in final draft.

$$p = a/n$$
$$\%\ \text{asbestos} = 100\,p$$

where

a = number of asbestos counts,

n = number of nonempty points counted (400).

The value reported should be rounded to the nearest percent.

If $a \geq 10$, 95 percent confidence intervals can be constructed about p by the equation

$$p \pm 1.96 \times \sqrt{\frac{pq}{n}}$$

where $q = 1-p$.

Example:

$$a = 60 \text{ points}$$
$$p = 60/400 = 0.15$$
$$q = 1 - 0.15 = 0.85$$
$$p \pm 1.96\sqrt{\frac{(0.15)(0.85)}{400}} = 0.15 \pm 0.018^{*}$$

Report: 15 ± 2%

8. References

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8. Personal communication, Walter C. McCrone.

*correct result is 0.15 ± 0.035.

9. Personal communication, Martin Rutstein.

10. Personal communication, James S. Webber.

11. Personal communication, Yachain Yaffe.

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Acknowledgment

This method is based in part on contributions and review comments of participants in the symposium "Methods definition for the polarized light microscope and x-ray diffraction analysis of bulk samples for asbestos," U. S. Bureau of Mines, Avondale Research Center, Avondale, Maryland, October 23-24, 1979.

X-RAY DIFFRACTION

1. Principle and Applicability

1.1 The theory of X-ray diffraction (XRD) is well-documented [1, 2]. Any solid, crystalline material will diffract an impingent beam of parallel, monochromatic X-rays whenever Bragg's Law,

$$\lambda = 2d \sin \theta,$$

is satisfied for a particular set of planes in the crystal lattice, where

λ = the X-ray wavelength, Å;

d = the interplanar spacings of the set of reflecting lattice planes, Å; and

θ = the angle of incidence between the X-ray beam and the reflecting lattice planes.

By appropriate orientation of a sample relative to the incident X-ray beam, an X-ray diffraction pattern can be generated that, in most cases, will be uniquely characteristic of both the chemical composition and structure of the crystalline phases present.

Unlike optical methods of analysis, however, XRD cannot determine crystal morphology. Therefore, in asbestos analysis, XRD does not distinguish between fibrous and nonfibrous forms of the serpentine and amphibole minerals (Table 1). However, when used in conjunction with optical methods such as polarized light microscopy (PLM), XRD techniques can provide a reliable analytical method for the identification and characterization of asbestiform minerals in bulk materials.

Bulk material samples are initially analyzed by PLM for identification and quantitation of asbestos. Subsequent analysis by XRD proceeds in two stages.

For qualitative analysis, samples are initially scanned over limited diagnostic peak regions for the serpentine (7.36 Å) and amphibole (8.3-8.5 Å) minerals (Table 2). Standard slow-scanning methods for bulk sample analysis may be used for materials shown by PLM to contain major amounts of asbestos (>5-10 percent). Detection of minor or trace amounts of asbestos may

TABLE 1. THE ASBESTOS MINERALS AND THEIR NONASBESTIFORM ANALOGS

Asbestiform	Nonasbestiform
SERPENTINE	
Chrysotile	Antigorite, lizardite
AMPHIBOLE	
Anthophyllite asbestos	Anthophyllite
Cummingtonite-grunerite asbestos ("Amosite")	Cummingtonite-grunerite
Crocidolite	Riebeckite
Tremolite asbestos	Tremolite
Actinolite asbestos	Actinolite

TABLE 2. PRINCIPAL LATTICE SPACINGS OF ASBESTIFORM MINERALS[a]

Minerals	Principal d-spacings (Å) and relative intensities			JCPDS Powder diffraction file [3] Number
Chrysotile	7.37_{100}	3.65_{70}	4.57_{50}	21-543[b]
	7.36_{100}	3.66_{80}	2.45_{65}	25-645
	7.10_{100}	2.33_{80}	3.55_{70}	22-1162 (theoretical)
"Amosite"	8.33_{100}	3.06_{70}	2.756_{70}	17-795* (nonfibrous)
	8.22_{100}	3.060_{85}	3.25_{70}	27-1170 (UICC)
Anthophyllite	3.05_{100}	3.24_{60}	8.26_{55}	9-455
	3.06_{100}	8.33_{70}	3.23_{50}	16-401 (synthetic)
Actinolite	2.72_{100}	2.54_{100}	3.40_{80}	25-157
Crocidolite	8.35_{100}	3.10_{55}	2.720_{35}	27-1415 (UICC)
Tremolite	8.38_{100}	3.12_{100}	2.705_{90}	13-437[b]
	2.706_{100}	3.14_{95}	8.43_{40}	20-1310[b] (synthetic)
	3.13_{100}	2.706_{60}	8.44_{40}	23-666 (synthetic mixture with richterite)

[a] This information is intended as a guide, only. Complete powder diffraction data, including mineral type and source, should be referred to, to insure, where possible, comparability of sample and reference materials. (In this regard, additional precision XRD data on amosite, crocidolite, tremolite, and chrysotile is expected to be available shortly, in a Bureau of Mines publication entitled "Chemical and Physical Characterization of Amosite, Chrysotile, Crocidolite, and Nonfibrous Tremolite for National Institute of Environmental Health Sciences Oral Ingestion Studies," by W. J. Campbell, C. W. Huggins, and A. G. Wylie.)

[b] Fibrosity questionable.

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*correct no. is 17-745.

require special sample preparation and step-scanning analysis of selected diagnostic peaks. All samples that exhibit diffraction peaks in the diagnostic peak regions for asbestiform minerals are submitted to a full (5°-60° 2θ; 1° 2θ/min) qualitative XRD scan and their diffraction patterns compared with standard reference powder diffraction patterns to verify initial peak assignments, and to identify possible matrix interferences when subsequent quantitative analysis will be performed.

Accurate quantitation of asbestos in bulk samples by XRD is critically dependent on particle size distribution, crystallite size, preferred orientation and matrix absorption effects, and comparability of standard reference and sample materials. The most intense diffraction peak that has been shown to be free from interference by prior PLM or qualitative XRD analysis is selected for quantitative determination of each asbestiform mineral.

A "thin-layer" method of analysis [4, 5] is recommended in which, subsequent to comminution of the bulk material to <10 µm by suitable cryogenic milling techniques, an accurately known amount of the sample is deposited on a silver membrane filter, and the mass of asbestiform material is determined by measuring the integrated area of the selected diffraction peak using a step-scanning mode, correcting for matrix absorption effects, and comparing with suitable calibration standards.

An alternative "thick-layer" or bulk method [6] may be used for semiquantitative analysis.

1.2 This method is applicable as a confirmatory method for identification and quantitation of asbestos in bulk material samples that have undergone prior analysis by PLM.

2. Range and Sensitivity

2.1. The range of the method has not been determined.

2.2. The sensitivity of the method has not been determined. It will be variable and dependent upon many factors, including matrix effects (absorption and interferences), diagnostic reflections selected, and their relative intensities.

3. Limitations

3.1. Interferences: The use of XRD for identification and quantitation of asbestiform minerals in bulk samples may be severely limited by the presence of other interfering materials in the sample. For naturally occurring materials the commonly associated asbestos-related mineral interferences can usually be anticipated. However, for fabricated materials the nature of the interferences may vary greatly (Table 3) and present more serious problems in identification and quantitation.

The interference problem is further aggravated by the variability of the silicate mineral powder diffraction patterns associated with alterations in the crystal lattice arising from differences in isomorphous substitution and degree of crystallinity. This variability often makes unambiguous identification of the asbestos minerals by comparison with standard reference diffraction patterns difficult. The amphiboles, for example, exhibit a wide variety of very similar chemical compositions, with the result being that their XRD patterns are characterized by having major (110) reflections of the monoclinic amphiboles and (210) reflections of the orthorhombic anthophyllite separated by less than 0.2 Å [8].

Common interferences are listed below.

3.1.1. The serpentine and amphibole minerals occur naturally in both fibrous and nonfibrous forms (Table 1). X-ray diffraction techniques, however, cannot distinguish between these two varieties. Therefore, in the absence of confirmatory PLM data, the identification of asbestos by XRD methods is not definitive. In addition, the presence of nonasbestiform serpentines and amphiboles in a sample will pose severe interference problems in the quantitative analysis of their asbestiform analogs, unless special sample preparation techniques and instrumentation are used [9].

3.1.2. Chlorite has major peaks at 7.19 Å and 3.58 Å that interfere with both the primary (7.36 Å) and secondary (3.66 Å) peaks for chrysotile; resolution of the primary peak to give good quantitative results may be possible when a step-scanning mode of operation is employed.

3.1.3. Halloysite has a peak at 3.63 Å that interferes with the secondary (3.66 Å) peak for chrysotile.

3.1.4. Kaolinite has a major peak at 7.15 Å that may interfere with the primary peak of chrysotile at 7.36 Å when present at concentrations of >10 percent. However, the secondary chrysotile peak at 3.66 Å may be used for quantitation.

TABLE 3. COMMON CONSTITUENTS IN INSULATION AND WALL MATERIALS [7]

A. Insulation materials

Chrysotile
"Amosite"
Crocidolite
*Rock wool
*Slag wool
*Fiber glass
Gypsum ($CaSO_4 \cdot H_2O$)
Vermiculite (micas)
*Perlite
Clays (kaolin)
*Wood pulp
*Paper fibers (talc, clay, carbonate fillers)
Calcium silicates (synthetic)
Opaques (chromite, magnetite inclusions in serpentine)
Hematite (inclusions in "amosite")
Magnesite
*Diatomaceous earth

B. Spray finishes or paints

Bassanite
Carbonate minerals (calcite, dolomite, vaterite)
Talc
Tremolite
Anthophyllite
Serpentine (including chrysotile)
Amosite
Crocidolite
*Mineral wool
*Rock wool
*Slag wool
*Fiber glass
Clays (kaolin)
Micas
Chlorite
Gypsum ($CaSO_4 \cdot H_2O$)
Quartz
*Organic binders and thickeners
Hydromagnesite
Wollastonite
Opaques (chromite, magnetite inclusions in serpentine)
Hematite (inclusions in "amosite")

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*Amorphous materials--contribute only to overall scattered radiation and increased X-ray background.

3.1.5. Gypsum has a major peak at 7.5 Å that overlaps the 7.33 Å peak of chrysotile when present as a major sample constituent.

3.1.6. Cellulose has a broad peak that partially overlaps the secondary (3.66 Å) chrysotile peak [6].

3.1.7. Overlap of both the primary and secondary peaks of crocidolite (8.35 Å, 3.10 Å) and amosite (8.33 Å, 3.06 Å) presents serious interference problems when these minerals occur in the presence of one another.

3.1.8. Carbonates may also interfere with quantitative analysis. $CaCO_3$ has a peak at 3.035 Å that overlaps the secondary peaks of crocidolite (3.10 Å) and amosite (3.06 Å) when present in concentrations of >5 percent. (Removal of carbonates with a dilute acid wash is possible; however, if present, chrysotile may be partially dissolved by this treatment [10].)

3.1.9. Interference between similarly spaced strong reflections of talc and anthophyllite will significantly reduce the sensitivity of the method for anthophyllite in the presence of talc. The anthophyllite peak at 8.9 Å is often masked by a strong talc peak at 9.3 Å. Similarly, talc peaks at 3.12 Å, 4.53 Å, and 4.56 Å interfere with anthophyllite peaks at 3.05 Å and 4.50 Å. For quantitation, the 8.26 Å of anthophyllite must be used.

3.1.10. A major talc peak at 3.12 Å also interferes with a primary tremolite peak at this same position and with secondary peaks of crocidolite and amosite. In the presence of talc, the 8.38 Å tremolite peak should be used for quantitation.

3.1.11. Overlap of peaks at 8.26 Å and 8.38 Å for anthophyllite and tremolite, interference when these minerals are analyzed in the presence of one another; however, adequate resolution may be attained in the step-scanning mode of operation.

3.2. Matrix Effects

3.2.1. If a Cu X-ray source is used, the presence of iron at high concentrations in a sample will result in significant X-ray fluorescence, leading to loss of peak intensity along with increased background intensity and an overall decrease in sensitivity. This situation may be corrected by choosing an X-ray source other than Cu; however, this is often accompanied

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both by loss of intensity and by decreased resolution of closely spaced reflections. Alternatively, use of a diffracted beam monochromator will reduce background fluorescent radiation, enabling weaker diffraction peaks to be detected.

3.2.2. X-ray absorption by the sample matrix will result in overall attenuation of the diffracted beam and may seriously interfere with quantitative analysis. Absorption effects may be minimized by using sufficiently "thin" samples for analysis [4, 11, 12]. However, unless absorption effects are known to be the same for both samples and standards, appropriate corrections should be made by referencing diagnostic peak areas to an internal standard [6] or filter substrate (Ag) peak [4, 5].

3.3. Particle Size Dependence: Because the intensity of diffracted X-radiation is particle-size dependent, it is essential for accurate quantitative analysis that both sample and standard reference materials have similar particle size distributions. The optimum particle size range for quantitative analysis of asbestos by XRD is 1 to 10 μm [13]. Comparability of sample and standard reference material particle size distributions should be verified by optical microscopy (or other suitable method) prior to analysis.

3.4. Preferred Orientation Effects: Preferred orientation of asbestiform minerals during sample preparation often poses a serious problem in quantitative analysis by XRD. A number of techniques have been developed for reducing preferred orientation effects in "thick layer" samples [6, 13]. However, for "thin" samples on membrane filters, the preferred orientation effects seem to be both reproducible and favorable to enhancement of the principal diagnostic reflections of asbestos minerals, actually increasing the overall sensitivity of the method [11, 15]. (Further investigation into preferred orientation effects in both thin layer and bulk samples and the utility of a sample spinner in minimizing these effects is required.)

3.5. Lack of Suitably Characterized Standard Materials: The problem of obtaining and characterizing suitable reference materials for asbestos analysis is clearly recognized. NIOSH has recently directed a major research effort toward preparation and characterization of analytical reference materials, including asbestos standards [14]; however, these are not available in large quantities for routine analysis.

In addition, the problem of ensuring comparability of standard reference and sample materials, particularly regarding crystallite size, particle size distribution, and degree of crystallinity, has yet to be adequately addressed. For example, Langer et al. [16] have observed that in insulating matrices, chrysotile tends to break open into bundles more frequently than amphiboles. This results in a line-broadening effect with a resultant decrease in sensitivity. Unless this effect is the same for both standard and sample materials, the amount of chrysotile in the sample will be underestimated by XRD analysis. To minimize this problem, it is essential that standardized matrix reduction procedures be used for both sample and standard materials.

4. Precision and Accuracy

4.1. Precision of the method has not been determined.

4.2. Accuracy of the method has not been determined.

5. Apparatus

5.1. Sample preparation apparatus requirements will depend upon the sample type under consideration and the kind of XRD analysis to be performed.

5.1.1 Mortar and Pestle: Agate or porcelain.

5.1.2. Sample Mill: SPEX, Inc., freezer mill, or equivalent.

5.1.3. Bulk Sample Holders

5.1.4. Silver Membrane Filters: 25-mm diameter, 0.45-µm pore size. Selas Corp. of America, Flotronics Div., 1957 Pioneer Road, Huntington Valley, PA 19006.

5.1.5. Microscope Slides

5.1.6. Vacuum Filtration Apparatus: Gelman No. 1107 or equivalent, and side-arm vacuum flash.

5.1.7. Microbalance

5.1.8. Ultrasonic Bath or Probe: Model W140, Ultrasonics, Inc., operated at a power density of approximately 0.1 W/mL, or equivalent.

5.1.9. Volumetric Flasks: 1-L volume.

5.1.10. Assorted Pipettes

5.1.11. Pipette Bulb

5.1.12. Nonserrated Forceps

5.1.13. Polyethylene Wash Bottle

5.1.14. Pyrex Beakers: 50-mL volume.

5.1.15. Desiccator

5.1.16. Filter Storage Cassettes

5.1.17. Magnetic Stirring Plate and Bars

5.1.18. Porcelain Crucibles

5.1.19. Muffle Furnace

5.2. X-Ray Diffraction Unit, equipped with:

5.2.1. Constant Potential Generator; Voltage and ma Stabilizers

5.2.2. Automated Diffractometer with Step-Scanning Mode

5.2.3. Copper Target X-Ray Tube: High intensity, fine focus, preferably.

5.2.4. X-Ray Pulse Height Selector

5.2.5. X-Ray Detector (with high voltage power supply): Scintillation or proportional counter.

5.2.6. Focusing Graphite Crystal Monochromator; or Nickel Filter (if Cu source is used, and iron fluorescence is not a serious problem).

5.2.7. Data Output Accessories:

5.2.7.1. Strip Chart Recorder
5.2.7.2. Decade Scaler/Timer
5.2.7.3. Digital Printer

5.2.8. Sample Spinner (optional).

5.2.9. Instrument Calibration Reference Specimen: α-quartz reference crystal (Arkansas quartz standard, Phillips) or equivalent.

6. Reagents

6.1. Standard Reference Materials: The reference materials listed below are intended to serve as a guide. Every attempt should be made to acquire pure reference materials that are comparable to sample materials being analyzed.

6.1.1. Chrysotile: UICC Canadian, or NIEHS Plastibest. (UICC reference materials available from: UICC, MRC Pneumoconiosis Unit, Llandough Hospital, Penarth, Glamorgan, CF61XW, UK).

6.1.2. Crocidolite: UICC; NIEHS (Dr. Jack Moore), Research Triangle Park, NC.

6.1.3. Amosite: UICC; NIEHS (Dr. Jack Moore), Research Triangle Park, NC.

6.1.4. Anthophyllite: UICC

6.1.5. Tremolite Asbestos: Wards Natural Science Establishment, Rochester, N.Y.; Cyprus Research Standard, Cyprus Research, 2435 Military Ave., Los Angeles, California 90064 (washed with dilute HCl to remove small amount of calcite impurity); India tremolite, Rajasthan State, India.

6.1.6. Actinolite Asbestos

6.2. Adhesive: Tape, petroleum jelly, etc. (for attaching silver membrane filters to holders).

6.3. Surfactant: 1 percent aerosol OT aqueous solution or equivalent.

6.4. Isopropanol: ACS Reagent Grade.

7. Procedure

7.1. Sampling: Samples for analysis of asbestos content shall be collected as specified in EPA Guidance Document #C0090, Asbestos-Containing Materials in School Buildings [7].

7.2. Analysis: All samples shall be analyzed initially for asbestos content by PLM. XRD shall be used as an auxiliary method when a second, independent analysis is requested.

Note: Asbestos is a toxic substance. All handling of dry materials should be performed in an operating fume hood.

7.2.1 Sample Preparation: The method of sample preparation required for XRD analysis will depend on: (1) the condition of the sample received (sample size, homogeneity, particle size distribution, and overall composition,

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as determined by PLM); and (2) the type of XRD analysis to be performed (qualitative, quantitative; thin layer or bulk).

Bulk materials are usually received as inhomogeneous mixtures of complex composition with very large particle size distributions. Preparation of a homogeneous, representative sample from asbestos-containing materials is particularly difficult because the fibrous nature of the asbestos minerals inhibits mechanical mixing and stirring, and because milling procedures may cause adverse lattice alterations.

Complete methods of sample preparation are detailed in the appropriate analytical sections. A discussion of specific matrix reduction procedures is given below.

7.2.1.1. Milling: Mechanical milling of asbestos materials has been shown to decrease fiber crystallinity, with a resultant decrease in diffraction intensity of the specimen; the degree of lattice alteration is related to the duration and type of milling process. Therefore, all milling times should be kept to a minimum.

For qualitative analysis, particle size is not, in general, of critical importance, and initial characterization of the material with a minimum of matrix reduction is often desirable to document the composition of the sample as received. Bulk samples of very large particle size (>2-3 mm) should be comminuted to <100 μm by careful grinding of all or a substantial portion of the original material in a mortar and pestle or other suitable mill (e.g., a microhammer mill or equivalent). When using a mortar and pestle for grinding, the sample should be moistened with ethanol, or some other suitable wetting agent, to minimize exposures.

For accurate, reproducible quantitative analysis, the particle size of both sample and standard materials should be reduced to 1 to 10 μm (Section 3.3). Dry ball milling at liquid nitrogen temperatures (e.g., Spex Freezer Mill, or equivalent) for a maximum time of ~10 min should be used to obtain satisfactory particle size distributions while protecting the integrity of the crystal lattice [4]. Bulk samples of very large particle size may require grinding in two stages for full matrix reduction to <10 μm [6,14].

Final particle size distributions should always be verified by optical microscopy or other suitable method.

7.2.1.2 Low Temperature Ashing: For materials shown by PLM to contain large amounts of cellulosic or other organic materials, it may be desirable to ash the samples prior to analysis to reduce background interference (see Section 7.2.2 of the PLM Method).

7.2.1.3. Removal of Carbonate Interferences: Because of the interference caused by some carbonates in the detection of asbestiform minerals by XRD (Section 3.1.9), it may be necessary to remove these interferents by a simple acid leaching procedure prior to analysis (Section 7.2.2 of the PLM Method).

7.2.1.4. All samples should be examined microscopically before and after each matrix reduction step to monitor changes in sample particle size, composition, and crystallinity, and to ensure sample representativeness and homogeneity for analysis.

7.2.2. Qualitative Analysis

7.2.2.1. Initial Screening of Bulk Material

The bulk material received may be either a "total" sample or a "single layer" sample. In either instance, initial qualitative analysis should be performed on a representative, homogeneous portion of the sample with a minimum of sample treatment.

1. Grind and mix the sample for 5 to 10 minutes with a mortar and pestle (or equivalent method, see Section 7.2.1.1.) to a final particle size of <100 µm.
2. Pack the sample into a standard bulk sample holder. Care should be taken to ensure that a representative portion of the milled sample is selected for analysis. Particular attention should be paid to avoid possible size segregation of the sample. (Note: Use of a back-packing method of bulk sample preparation may reduce preferred orientation effects.)
3. Mount the sample on the diffractometer and scan over the diagnostic peak regions for the serpentine (7.36 Å) and amphibole (8.3-8.5 Å) minerals (see Table 2). The X-ray diffraction equipment should be optimized for intensity. A slow scanning speed of 1° 2θ/min is recommended for adequate resolution. Use of a sample spinner is optional.

4. Submit all samples that exhibit diffraction peaks in the diagnostic regions for asbestiform minerals to a full qualitative XRD scan (5°-60° 2θ; 1° 2θ/min) to verify initial peak assignments and to identify potential matrix interferences when subsequent quantitative analysis is to be performed.
5. Compare the sample XRD pattern with standard reference powder diffraction patterns (i.e., JCPDS PDF data [3] or those of other well-characterized reference materials). Principal lattice spacings of asbestiform minerals are given in Table 2; common constituents of bulk insulation and wall materials are listed in Table 3.

7.2.2.2. Detection of Minor or Trace Constituents: Routine screening of bulk materials by XRD may fail to detect small concentrations (<5 percent) of asbestos. The limits of detection will, in general, be improved if matrix absorption effects are minimized, and if the sample particle size is reduced to the optimal 1 to 10 μm range, provided that the crystal lattice is not degraded in the milling process. Therefore, in those instances where confirmation of the presence of an asbestiform mineral at very low levels is required, or where a negative result (Section 7.2.2.1) is in conflict with previous PLM results, it may be desirable to prepare the sample as for quantitative analysis (Section 7.2.3) and step-scan over appropriate 2θ ranges of selected diagnostic peaks (Table 2). (Accurate transfer of the sample to the silver membrane filter is not necessary unless subsequent quantitative analysis is to be performed).

7.2.2.3. Identification of Discrete Sample Phases

In some instances, confirmatory identification of discrete sample phases (i.e., bundles of fibers) by XRD may be necessary. The following procedure is recommended.

1. If necessary, reduce sample particle size to <100 μm by a suitable grinding method (Section 7.2.1.1).
2. Spread a small amount of the sample on a microscope slide, or deposit on a silver membrane filter. If enough sample is available, a standard bulk sample holder may be used for sample preparation (Section 7.2.2.1).

3. Analyze according to the procedure described in Section 7.2.2.1.

7.2.3. Quantitative Analysis: The proposed method for quantitation of asbestos in bulk samples is a modification of the NIOSH-recommended thin-layer method for chrysotile in air [5]. (The thick-layer method of M. Taylor may be used for semiquantitative analysis [6]. However, this requires the addition of an internal standard, use of a specially fabricated sample press, and relatively large amounts of standard reference materials. Additional research is required to evaluate the comparability of thin- and thick-layer methods for quantitative asbestos analysis.)

7.2.3.1. Mill and size all or a substantial representative portion of the sample as outlined in Section 7.2.1.1.

7.2.3.2. Dry in a 100° C oven for 2 hr; cool in a desiccator.

7.2.3.3. Weigh accurately to the nearest 0.01 mg.

7.2.3.4. Samples shown by PLM to contain large amounts of cellulosic or other organic materials, and/or carbonates, should be submitted to appropriate matrix reduction procedures described in Sections 7.2.1.2 and 7.2.1.3. After ashing and/or acid treatment, repeat the drying and weighing procedures described above, and determine the percent weight loss, L.

7.2.3.5. Quantitatively transfer an accurately weighed amount (50-100 mg) of the sample to a 1-L volumetric flask with approximately 200 mL isopropanol to which 3 to 4 drops of surfactant have been added.

7.2.3.6. Ultrasonicate for 10 min at a power density of approximately 0.1 W/mL, to disperse the sample material.

7.2.3.7. Dilute to volume with isopropanol.

7.2.3.8. Place flask on magnetic stirring plate. Stir.

7.2.3.9. Place a silver membrane filter on the filtration apparatus, apply a vacuum, and attach the reservoir. Release the vacuum and add several milliliters of isopropanol to the reservoir. Vigorously hand shake the asbestos suspension and immediately withdraw an aliquot from the center of the suspension so that total sample weight, W_T, on the filter will be approximately 0.1 mg.* Do not adjust the volume in the pipet by expelling part of the suspension; if more than the desired aliquot is withdrawn, discard the aliquot and resume the procedure with a clean pipet. Transfer the aliquot to the reservoir. Filter rapidly under vacuum. Do not wash reservoir walls. Leave filter apparatus under vacuum until dry. Remove reservoir, release vacuum, and remove filter with forceps.

---

*correct amount is ca. 1.0 mg.

7.2.3.10. Attach the filter to a flat holder with suitable adhesive and place on the diffractometer. Use of a sample spinner is optional.

7.2.3.11. For each asbestos mineral to be quantitated select a reflection (or reflections) that has been shown to be free from interferences by prior PLM or qualitative XRD analysis and that can be used unambiguously as an index of the amount of material present in the sample (see Table 2).

7.2.3.12. Analyze the selected diagnostic reflection(s) by step scanning in increments of 0.02° 2θ for an appropriate fixed time and integrating the counts. (A fixed count scan may be used alternatively; however, the method chosen should be used consistently for all samples and standards.) An appropriate scanning interval should be selected for each peak, and background corrections made. For a fixed time scan, measure the background on each side of the peak for one-half the peak-scanning time. The net intensity, I_a, is the difference between the peak integrated count and the total background count.

7.2.3.13. Determine the net count, I_{Ag}, of the filter 2.36 Å silver peak following the procedure in Section 7.2.3.12. Remove the filter from the holder, reverse it, and reattach it to the holder. Determine the net count for the unattenuated silver peak, I°_{Ag}. Scan times may be less for measurement of silver peaks than for sample peaks; however, they should be constant throughout the analysis.

7.2.3.14. Normalize all raw, net intensities (to correct for instrument instabilities) by referencing them to an external standard (e.g., the 3.34 Å peak of an α-quartz reference crystal). After each unknown is scanned, determine the net count, $\overset{\circ}{I}_r$, of the reference specimen following the procedure in Section 7.2.3.12. The normalized intensities are determined by dividing the peak intensities by $\overset{\circ}{I}_r$:

$$\hat{I}_a = \frac{I_a}{\overset{\circ}{I}_r}, \quad \hat{I}_{Ag} = \frac{I_{Ag}}{\overset{\circ}{I}_r}, \quad \text{and} \quad \hat{I}^{\circ}_{Ag} = \frac{I^{\circ}_{Ag}}{\overset{\circ}{I}_r}$$

8. Calibration

8.1. Preparation of Asbestos Standards

8.1.1. Mill and size standard asbestos materials according to the procedure outlined in Section 7.2.1.1. It is essential that equivalent, standardized matrix reduction and sizing techniques be used for both standard and sample materials.

8.1.2. Dry in a 100° C oven for 2 hr; cool in a desiccator.

8.1.3. Prepare two suspensions of each standard in isopropanol by weighing approximately 10 and 50 mg of the dry material to the nearest 0.01 mg. Quantitatively transfer each to a 1-L volumetric flask with approximately 200 mL isopropanol to which a few drops of surfactant have been added.

8.1.4. Ultrasonicate (at 5 W power, or equivalent) for 10 min to disperse the asbestos material.

8.1.5. Dilute to volume with isopropanol.

8.1.6. Place flask on magnetic stirring plate. Stir.

8.1.7. Prepare, in triplicate, a series of at least five standard filters to cover the desired analytical range, using appropriate aliquots of the 10 and 50 mg/L suspensions.

Mount a filter on the filtration apparatus. Place a few milliliters of isopropanol in the reservoir. Vigorously hand shake the asbestos suspension and immediately withdraw an aliquot from the center of the suspension. Do not adjust the volume in the pipet by expelling part of the suspension; if more than the desired aliquot is withdrawn, discard the aliquot and resume the procedure with a clean pipet. Transfer the aliquot to the reservoir. Keep the tip of the pipet near the surface of the isopropanol. Filter rapidly under vacuum. Do not wash down the sides of the reservoir. Leave the vacuum on for a time sufficient to dry the filter. Release the vacuum and remove the filter with forceps.

8.1.8. Mount the filter on a flat holder. Perform step scans on selected diagnostic reflections of the standards and reference specimen using the procedures outlined in Section 7.2.3.2. and the same conditions as those used for the samples.

8.1.9. Determine the normalized intensity for each peak measured, $\hat{I}^{\circ}_{c}$, as outlined in Section 7.2.3.14.

9. Calculations

9.1 For each asbestos reference material, calculate the exact weight deposited on each standard filter from the concentrations of the standard suspensions and aliquot volumes. Record the weight, w, of each standard. Prepare a calibration curve by regressing $\hat{I}^{\circ}_{c}$ on w. Poor reproducibility (±15 percent RSD) at any given level indicates problems in the sample preparation technique, and a need for new standards. The data should fit a straight line equation.

9.2. Determine the slope, m, of the calibration curve in counts/microgram. The intercept, b, of the line with the $\hat{I}^{\circ}_{c}$ axis should be approximately 0. A large negative intercept indicates an error in determining the background. This may arise from incorrectly measuring the baseline or from interference by another phase at the angle of background measurement. A large positive intercept indicates an error in determining the baseline or that an impurity is included in the measured peak.

9.3. Using the normalized intensity, $\hat{I}_{Ag}$, for the attenuated silver peak of a sample, and the corresponding normalized intensity from the unattenuated silver peak, $\hat{I}^{\circ}_{Ag}$, of the sample filter, calculate the transmittance, T, for each sample as follows [17, 18]:

$$T = \frac{\hat{I}_{Ag}}{\hat{I}^{\circ}_{Ag}}$$

9.4. Determine the correction factor, f(T), for each sample according to the formula:

$$f(T) = \frac{-R \ln T}{1-T^{R}}$$

where

$$R = \frac{\sin \theta_{Ag}}{\sin \theta_{a}} ,$$

θ_{Ag} = angular position of the measured silver peak (from Bragg's Law), and

θ_a = angular position of the diagnostic asbestos peak.

9.5. Calculate the weight, in micrograms, of the asbestos material analyzed for in each sample, using the appropriate calibration data and absorption corrections:

$$W_a = \frac{\hat{I}_a - b}{m} \times f(T)$$

9.6 Calculate the percent composition, P_a, of each asbestos mineral analyzed for in the parent material, from the total sample weight, W_T, on the filter:

$$P_a = \frac{W_a\,(1-.01L)}{W_T} \times 100$$

where

P_a = percent asbestos mineral in parent material;
W_a = mass of asbestos mineral on filter, in μg;
W_T = total sample weight on filter, in μg;
L = percent weight loss of parent material on ashing and/or acid treatment (Section 7.2.3.1).

10. References

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Acknowledgment

This method is based in part on contributions and review comments of participants in the symposium "Methods definition for the polarized light microscope and x-ray diffraction analysis of bulk samples for asbestos," U.S. Bureau of Mines, Avondale Research Center, Avondale, Maryland, October 23-24, 1979.

APPENDIX C

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APPENDIX D

INSTRUCTIONS AND REPORTING FORMS

RESEARCH TRIANGLE INSTITUTE
POST OFFICE BOX 12194
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27709

March 28, 1980

Mr. Carl Melton
Battelle Columbus Laboratory
505 King Ave.
Columbus, Ohio 43201

Dear Mr. Melton:

Your laboratory has indicated a willingness to test the tentative EPA methods for identification and quantitation of asbestos in bulk materials. Enclosed please find a third draft of the proposed methods and a selection of samples chosen to characterize their accuracy and precision. These methods must be followed carefully for your results to provide a meaningful reflection of the potential of the methods. Note in detail any deviation in your application of the method. Should you so desire, compare the results obtained by this method with those obtained using your laboratory's standard procedures. We will welcome any comments on the procedures. Testing must be performed and reported (received) no later than April 21, 1980, to be useful in this draft's evaluation. EPA has authorized a standard payment of $20 per sample for the polarized light microscope results and $40 per sample for X-ray diffraction results received by that date.

Should there be any question in this matter or should you find your laboratory unable to respond as requested, please contact me or Gene Brantly immediately at 1-800-334-8571, ext. 6745.

Thank you for your continued interest in the methods development program.

Sincerely yours,

D. E. Lentzen

D. E. Lentzen, Ph.D.
Environmental Scientist

DEL/lb

(919) 541-6000 FROM RALEIGH DURHAM AND CHAPEL HILL

TENTATIVE METHOD FOR THE DETERMINATION OF ASBESTIFORM MINERALS IN BULK SAMPLES BY POLARIZED LIGHT MICROSCOPY

Validation Study

Laboratory:______________________________ RTI Sample #:_____________

Analyst:
Analytical method:

Gross sample appearance: ____
____
____

Subsampling, matrix reduction or sample preparation steps: ___________
____
____
____

FIBER IDENTIFICATION

Are fibers present? YES NO
For all fiber types, complete the following:

	TYPE 1	TYPE 2
Extinction characteristics:	____________	____________
Sign of elongation:	____________	____________
Refractive indices:	____________ ____________	____________ ____________
Fiber morphology, color:	____________ ____________	____________ ____________
Fiber identity:	____________ ____________	____________ ____________

QUANTITATION

Magnification used:

Number of non-empty points counted (n) = 400

Points counted for asbestos fibers (a) =

Relative area occupied by asbestos $(p=a/n)$ =

$q = 1-p$ =

95% confidence intervals $(p \pm 1.96\ pq/n)$ =

Reported percent asbestos: _____________

COMMENTS

____
____
____
____

Reviewed by:__________________________________

INSTRUCTIONS

ANALYSIS OF BULK MATERIALS BY X-RAY POWDER DIFFRACTION

1. Validation of the quantitative XRD method is an important objective of this study. We recognize, however, that lack of suitable reference materials may present a problem to some laboratories. For the purposes of this study, please proceed with the quantitation using the standard materials available and report all raw data, along with the final results, as requested on the report form.

   It should be emphasized that this study is intended to validate the XRD method independent of the PLM method. If prior analysis by PLM has been done, do not let these results influence the outcome of the XRD analysis.

2. Complete one data form for each sample analyzed. If multiple measurements are made on a single sample, report individual results on separate data forms; do not average results.

3. All deviations from the proposed method should be noted where appropriate.

4. Details of matrix reduction steps should include equipment specifications (e.g., type of grinding mill) and the length of time for each procedure where appropriate.

5. All calibration curves, diffractograms, and intensity data must be included, as requested, for accurate assessment of reported results.

6. Please include any comments you may have on this method. In particular, compare with your standard XRD method, note specific problem areas, and detail recommendations for improvement. If you so desire, analyze the samples by your standard XRD method (report results on the data forms provided, noting deviation from proposed method), and compare your results with those obtained by the proposed method.

X-RAY POWDER DIFFRACTION ANALYSIS REPORT

Laboratory ________________________ Date ____________

I. SAMPLE IDENTIFICATION

Sample Label or # as Received: ________________________
Laboratory # Assigned: ________________________
Gross Sample Appearance: ________________________

II. EXPERIMENTAL

Matrix Reduction or Sample Preparation: ________________________
____
____

Particle Sizing: Method ________________________
Final Particle Size Distribution (range, mmd) μm _____
Mounting Media: ________________________
Type(s) of Analysis: ___Quantitative ___Semiquantitative __Qualitative
Sample Spinner: _____yes ____no
External Reference Standard (type. source, reference peak 2θ): _________
Calibration Standard Material(s) (asbestos type, source, matrix reduction, final particle size): ________________________
____

III. RESULTS

Please attach copies of:

1. Calibration curves, including regression equations, and
2. All diffractograms, appropriately labeled with sample or standard #; X-ray source (type, wavelength); kV; ma; filter or monochromator used; collimator slit widths; scanning speed (specify step width and fixed time or count for step-scanning); time constant; chart speed; and attenuation. All scans must be accurately indexed (2θ), with exact scanning intervals noted.

Asbestos Present: __Yes __No
Confirmed by PLM: __Yes __No

Other Materials Present and %: ______
____
____

	Type 1	Type 2
Asbestos Indentification	_____	_____
Major Peaks (2θ)	_____ _____ _____	_____ _____ _____
Diagnostic peak (2θ)	_____	_____
Integrated peak area, I_a, (cps)	_____	_____
Reference peak area, I_r, (cps)	_____	_____
Absorption correction, f(T)	_____	_____
Sample weight, W_T, (μg)	_____	_____
% Wt loss on ashing or acid wash, L	_____	_____
Mass of asbestos on filter, Wa, (μg)	_____	_____
% Asbestos, Pa	_____	_____
Estimated error	_____	_____

____
____
Major Peaks Unaccounted For: ___
____

Analyst: ________________________

Comments: ________________________
____
____
____
____
____
____
____

APPENDIX E

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PARTICIPANTS IN RESEARCH TRIANGLE INSTITUTE SPONSORED SYMPOSIUM ON "METHODS DEFINITION FOR THE POLARIZED LIGHT MICROSCOPE AND X-RAY DIFFRACTION ANALYSIS OF BULK SAMPLES FOR ASBESTOS" HELD AT THE U.S. BUREAU OF MINES, AVONDALE RESEARCH CENTER, AVONDALE, MARYLAND

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